

The Extractive Metallurgy of Zinc

by Roderick J Sinclair

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PART A

GENERAL CONTEXT

This part of the text covers the general structure of the zinc smelting industry including its scope, an historical background and details of the source materials used for the extraction of primary zinc metal.

Chapter 1	Industry Perspective and Introduction
Chapter 2	Historical Background
Chapter 3	Raw Materials

Zinc Smelting Industry Perspective and Introduction

INTRODUCTION

Zinc is a common base metal with diverse uses in a modern society. It is used for fabrication of metal components in the form of diecasting alloys and as brasses where it is alloyed with copper. Its major use is for the corrosion protection or galvanising of steel, and it achieves this protection by forming a surface barrier as well as by corroding preferentially to the underlying steel. Zinc also has uses as an oxide in the formulation of rubber, for use in fertilisers and for various minor pharmaceutical and medical uses. It is an essential element for life and a natural part of the environment.

World zinc consumption grew from around five million tonne per year in 1970 to over eight million tonne per year by the end of the 20th century and to 9.7 million tonne per year in 2003. This represents a growth rate of the order of two per cent per year. Around one third of consumption is derived from recycled materials and this proportion is growing as more emphasis is given to environmental issues and the recycle and re-use of resources. A large portion of the recycled material is in the form of brass scrap (40 per cent) and the remainder is diecasting and other metallic scrap or processing residues such as galvanising drosses and steel plant dusts from the recycle of scrap steel.

Zinc demand is closely linked to general economic activity, although as a mature commodity, intensity of use (expressed as tonnes of consumption per dollar of GDP) has declined. World intensity of use was around 250 tonne per US\$ billion in the year 2000, but this figure varies greatly between different countries, reflecting different positions on the economic development cycle.

Primary zinc metal is produced predominantly by the smelting of zinc sulfide concentrates. A few smelters are based on oxide feeds derived from unique orebodies containing zinc silicates or zinc carbonates, but these represent only 3.5 per cent of total primary zinc production and are special cases. Details of raw materials and requirements as process feed are given in Chapter 3.

Zinc mining and smelting tend to be separately concentrated and the distribution of these production activities, as at the year 2003, is shown in Table 1.1.

TABLE 1.1
Distribution of world zinc mining and smelting activities.

Region	Distribution of Mines	Distribution of Smelters
Europe (including Eastern Europe)	10%	27%
Africa	3%	2%
Canada	15%	10%
USA	6%	3%
South America (including Mexico)	19%	7%
China	27%	28%
Other Asia (including Japan/ Korea)	5%	17%
Australia	15%	6%

From Table 1.1 there is clearly an imbalance between regional mining and smelting activities, indicating considerable trade in the intermediate smelter feed or zinc concentrate.

THE ZINC SMELTING INDUSTRY

The world primary zinc smelting industry employs five distinctive processes:

1. Electrolytic Process (Roast – Leach – Electrowin),
2. Imperial Smelting Process or ISF (blast furnace),
3. Vertical Retort Process,
4. Electrothermic Retort Process, and
5. Horizontal Retort Process.

The older horizontal retort process was the main method of zinc smelting at the beginning of the 20th century but had virtually been totally superseded at the end of that century.

The other retorting processes are also rapidly declining, except for the processing of secondary materials, leaving primary production to the Imperial Smelting Furnace (ISF) and electrolytic plants. The ISF smelters process both sulfide concentrates and secondary oxidic materials, and in fact require low cost secondary feeds to be competitive with the Electrolytic Process.

The proportion of total world primary zinc production contributed by each of the process types are given in Table 1.2.

TABLE 1.2
Relative contribution of different smelting processes.

Process Type	Horizontal Retort	Vertical Retort	Electrothermic Retort	ISF	Electrolytic
1950	55%	7%	6%	0%	32%
1970	5%	9%	4%	9%	73%
1990	0%	3%	3%	13%	81%
2000	0%	3%	2%	12%	83%
2003	0%	2%	1.5%	7.5%	89%
Number of plants -2003	0	2	1	10	86

Clearly, from Table 1.2, the electrolytic process predominates with close to 89 per cent of production by the end of 2003. The ISF Process has not grown in total capacity in the last decade and has difficulty competing without access to low cost feeds. The number of operating plants is in decline.

As at the end of 2003, there were 86 electrolytic zinc plants in operation worldwide (see Table 1.3) with a total capacity of 9.2 million tonne per year. Since the mid 1990s there has been a large increase in smelting capacity in China with many small production units. This is in contrast to the trend towards expansion to larger capacity smelters in Western economies. Relevant capacity statistics are as follows:

	Rest of World	China
Median capacity	103 000 t/a	40 000 t/a
First quartile capacity	62 000	20 000
Third quartile capacity	153 000	63 000
Maximum capacity	460 000	350 000

The capacity distribution of world plants is shown in Figure 1.1 as the cumulative capacity of all plants above a given size.

Figure 1.1 indicates that 70 per cent of world capacity is contributed by plants above 100 000 tonne per annum, and 45 per cent of world capacity by plants above 200 000 tonne per annum, of which there are 17. There are only three plants listed with capacities above 300 000 tonne per annum.

Figure 1.1 also suggests that there are capacity breaks at around 150 000 and 250 000 tonne per annum, as preferred plant sizes under conditions prevailing in the year 2003. This approximately corresponds with practical sizes of major equipment – in particular roasting units and electrolysis units.

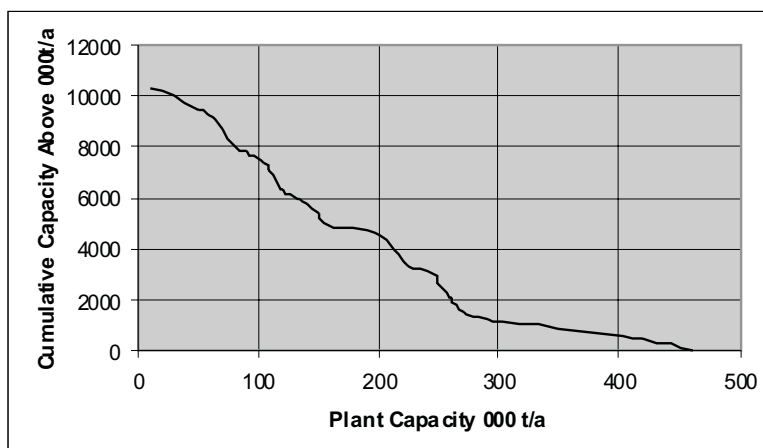


FIG 1.1 -Distribution of world electrolytic capacity.

There are 99 plants listed in Tables 1.3 and 1.4, of which 86 use the electrolytic process. The capacity distribution of these plants is shown in Figure 1.2 and clearly illustrates the relatively large number of small capacity units operating in China in comparison with the rest of the world.

Although all major metal production methods are reviewed, the primary emphasis of this text is on the technology associated with the Electrolytic Zinc Process. Other processes principally involve the reduction of zinc oxides by carbon at elevated temperatures – or carbothermic reduction, and form zinc metal in the vapour state. The Imperial Smelting Process is the dominant form of carbothermic reduction. Apart from this there have been many other processes, some forming metal directly by vapour condensation and others reoxidising the zinc vapour to a zinc oxide fume that can be a feed source to the electrolytic process or the ISF. The fuming approach is generally applied to the treatment of low grade oxidised ores, residues or other secondary materials and the process is essentially used as a means of separation and concentration of zinc values. The starting materials must have low value to carry the cost of this concentration step as well as final reduction and recovery of zinc metal.

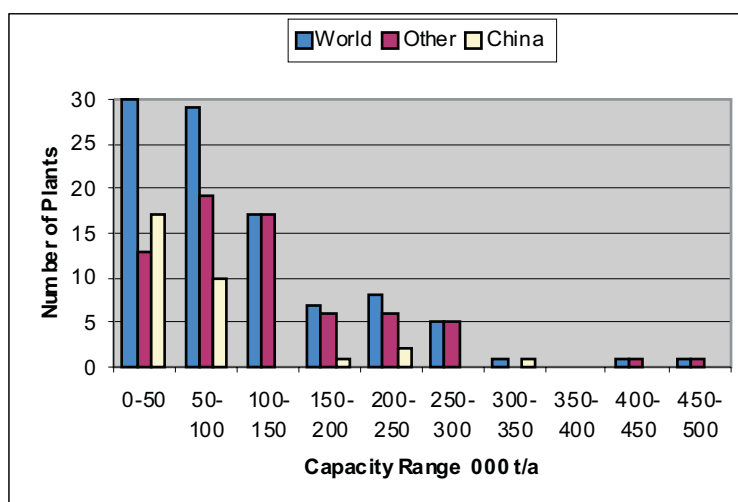


FIG 1.2 - World zinc plants – capacity distribution.

Carbothermic reduction processes, which produce zinc metal directly by condensation from the vapour phase, generally give a low-grade product metal, usually heavily contaminated with lead and cadmium and requiring an additional refining stage.

PROCESS PRINCIPLES – ELECTROLYTIC ZINC PROCESS

The generally applied form of the Electrolytic Zinc Process is based on a sulfate system using zinc sulfate solution for electrolysis. Other systems are possible but are not commercially used to any significant extent. These systems are discussed in Chapter 10. The basic flow sheet of the process is shown in Figure 1.3.

The preparation of zinc sulfate solution utilises recycled sulfuric acid as spent electrolyte and may take many forms depending on the feed material. If the smelter's raw feed is an oxidised material then simple dissolution in the acid spent electrolyte is practical. Most commonly, raw materials are zinc sulfide concentrates and the most common preparatory step is to roast the sulfides to eliminate sulfur as SO_2 gas and convert the zinc mineralisation to zinc oxide. Roasting is most commonly conducted in a fluid bed roaster at 900 to 1000°C. Roaster gases are washed, and are then converted to sulfuric acid, as a by-product, using the Contact Process. Details of roasting operations are given in Chapter 4.

During roasting, iron sulfides are also converted to oxides and combine with zinc oxide to form zinc ferrite. Ferrites are insoluble in dilute sulfuric acid solution and require elevated temperatures and reasonably strong acid conditions to be attacked. Iron is dissolved as a result and must then be removed from the leach solution before it is suitable for electrolysis.

The solution preparation step thus generally involves a number of progressively more aggressive leaching stages and an iron separation stage. There are many variations of the flow sheet for solution preparations along these lines covered in Chapter 5, but a typical approach is shown in Figure 1.4.

Other methods of solution preparation involve the direct leaching of sulfides in a sulfuric acid solution under oxidising conditions. This may be under pressure at elevated temperatures, or at atmospheric pressure using an oxidation catalyst such as ferric iron in solution. The aim with direct leaching is to convert the bulk of the sulfide sulfur to elemental sulfur, which may be recovered. This approach enables a closed sulfate solution circuit to be used. Sulfides can be oxidised fully to sulfate, but then sulfate rejection from solution is necessary, usually by lime neutralisation and rejection as gypsum. This adds considerable cost over a closed circuit system.

The key to successful and efficient electrolytic deposition of zinc is the purification of the electrolyte and the removal of all impurities more electropositive than zinc and which will deposit on the cathode in preference to zinc. Apart from contamination of the zinc deposit, many such impurities have low hydrogen overvoltages and allow the preferential deposition of hydrogen rather than zinc.

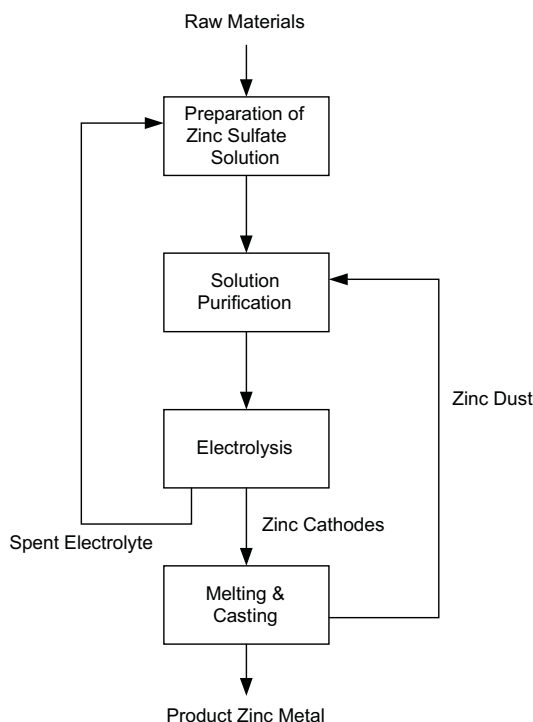


FIG 1.3 - General flow sheet for the electrolytic zinc process.

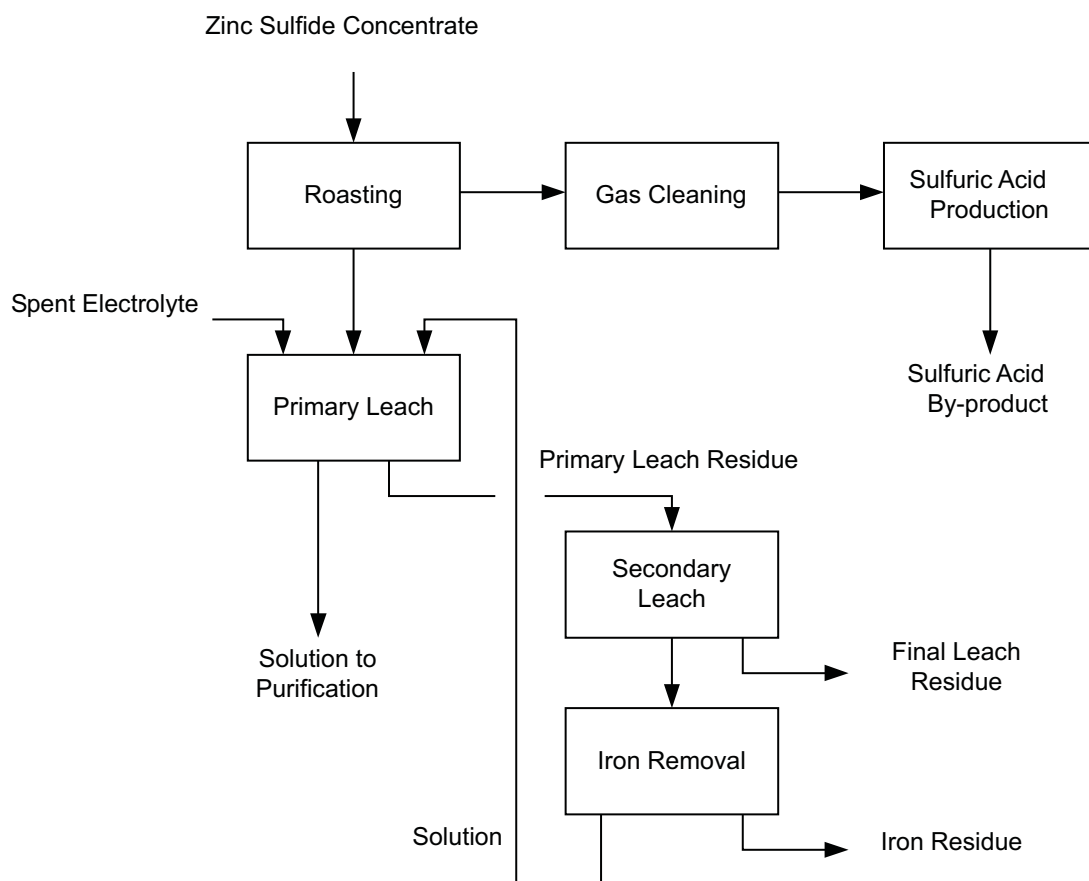


FIG 1.4 - Typical roasting-leaching flow sheet.

This leads to low process (or current) efficiency. Consequently, the removal of these impurities by cementation on zinc dust is used for solution purification. Purification often uses three stages with varying conditions and the use of activators to remove the full range of deleterious impurities. Solution purification details are given in Chapter 6.

Electrolysis is carried out in open tank cells using parallel plate lead anodes and aluminium cathodes. Cathodes are lifted from the cells periodically (usually every 48 hours), the zinc deposit is stripped off and the clean sheet is returned. The handling and stripping of cathodes are highly automated operations in a modern zinc plant. Details of the electrolysis operation are covered in Chapter 7.

Stripped zinc is melted in an electric induction furnace and is cast into ingots either with or without prior addition of alloying elements. Details are covered in Chapter 8.

The following chapters discuss details of these basic steps of the process as indicated, including the basic chemistry involved, the processing options, and the preferred operating conditions and controls. The requirements for handling effluents and mass balance control have also been covered, together with details of energy consumption in Chapter 20 and general aspects of costs and economics of the electrolytic process in Chapter 21.

A listing of world electrolytic zinc plants showing capacities at the year 2000 and the date of commencement of operations is given in Table 1.3.

TABLE 1.3*World primary electrolytic zinc plant in 2003.**(Source: International Zinc Association, International Lead Zinc Study Group.)*

Country and Company Name	Location	Year First Operated	Annual Capacity (tonnes)
EUROPE			
BELGIUM Union Minière SA	Balen (Anvers)	1934	255 000
BULGARIA KSM Dimitar Blagoev KSM Dimitar Blagoev	Kardjali Plovdiv	1956 1961	30 000 62 000
FINLAND Outokumpu Zinc Oy	Kokkola	1969	260 000
FRANCE Union Minière SA	Auby	1975	245 000
GERMANY Metaleurop Weser Zink Ruhr Zink	Nordenham Datteln	1972 1968	135 000 120 000
ITALY Eniressorse	Porto Vesme	1984	110 000
NETHERLANDS Zinifex	Budel-Dorplein	1974	220 000
NORWAY Norzinc AS	Eitheim-Odda	1929	145 000
POLAND ‘Boleslaw’	Krakow	1955	73 000
PORTUGAL RMC - Portugal	Quimigal	1980	12 000
RUSSIA Electrozinc Tscheliabinsk Zinc	Vladikavkaz Tscheliabinsk	1934 1935	90 000 200 000
SERBIA ‘Trepca’	Titova Microvica	1968	70 000
SPAIN Asturiana de Zinc SA Espanola de Zinc SA	Aviles Cartegena	1960 1960	460 000 45 000
TURKEY Cinko-Kursun Metal Sanyii	Kayseri	1976	38 000
UKRAINE ‘Ukrzink’	Konstantinovka	1930	25 000
AFRICA			
ALGERIA Soc Nat de Siderurgie	Ghazaouet	1975	40 000
SOUTH AFRICA Zincor	Vogelstruisbult (Springs)	1969	118 000
NAMIBIA Skorpion Zinc	Rosh Pinah	2003	150 000
NORTH AMERICA			
CANADA Canadian Electorlytic Zinc Cominco Hudson Bay M&S Co Falconbridge	Valleyfield Trail, BC Flin Flon Kidd Creek	1963 1916 1930 1972	260 000 290 000 114 000 145 000

USA			
Big River Zinc (Korea Zinc)	Sauget	1941	105 000
Zinifex	Clarksville	1978	115 000
SOUTH AMERICA			
ARGENTINA			
Sulfacid SA	Fray Luis Beltran	1963	39 000
BRAZIL			
Cia Mercantil and Industrial	Itagui	1965	62 000
Cia Mineira de Metais	Tres Marias	1969	160 000
Cia Paraibuna de Metais	Juiz de Fora	1980	92 000
MEXICO			
Industrial Minera Mexico	San Luis Potosi	1982	114 000
Met-Mex Peñoles	Torreon	1974	225 000
PERU			
Centromin Peru	La Oroya	1951	80 000
Cominco	Cajamarquilla	1981	120 000
ASIA			
CHINA			
North West Lead & Zinc	Baiyin (Gansu)	1991	200 000
Huludao Zinc Smelter	Huludao (Liaoning)		165 000
Zhuzhou Lead Zinc Smelter	Zhuzhou (Hunnan)	1959	350 000
Luizhou Longchen Chemical	Guangxi		60 000
Baoji Dongling	Shuikoushan		60 000
Huize Lead Zinc Smelter	Huize (Yunnan)		55 000
Fengxian Zinc Products	Shaanxi		60 000
Hongda Chemical	Sichuan		60 000
Luizhou Zinc Company	Luizhou		90 000
Sanii Group	Hunan		60 000
Xingwang Zinc Industry	Shaanxi		50 000
Huidong Lead Zinc Industry	Huidong		35 000
Kaifeng Kaihua Group	Henan		40 000
Luizhou Chem & Met Corp	Laibin		36 000
16 plants below 35 000 t/a	Various locations		306 000
INDIA			
Binani Zinc	Cochin (Kerala)	1967	30 000
Hindustan Zinc	Debari (Udaipur)	1968	71 000
	Vishakhapatnam	1977	50 000
IRAN			
Calcamine Company	Bandar Abbas	2000	43 000
Bafg	Yasd		30 000
National Iranian Lead Zinc	Zanjan		15 000
Faravani Mawed Nadani	Dandi		10 000
JAPAN			
Akita Zinc Co	Iilima	1972	200 000
Hikoshima Smelting Co	Hikoshima	1970	84 000
Kamoika M&S Co	Kamioka	1943	72 000
Toho Zinc Co	Annaka	1937	140 000
KAZAKHSTAN			
Kazpolymetal	Ust Kamenogorsk	1948	249 000
Leninogorsk Polimetal	Leninogorsk	1966	109 000
SOUTH KOREA			
Korea Zinc Co	Onsan	1978	420 000
Young Poon Corp	Sukpo	1971	270 000
NORTH KOREA			
	Munpyong	1960	150 000
	Nampo	1935	60 000
	Danchon	1985	50 000
THAILAND			
Padaeng Industries	Tak	1985	105 000

UZBEKISTAN Almalyk M&M Combine	Almalyk	1971	120 000
AUSTRALIA Zinifex	Hobart	1916	245 000
	Port Pirie	1968	40 000
Korea Zinc Co	Townsville	2001	200 000

PROCESS PRINCIPLES – CARBOTHERMIC REDUCTION

Most pyrometallurgical processes involve the reduction of zinc oxide contained in a solid phase with CO to produce zinc metal in vapour form, which is removed from the reaction zone in the exit gas stream. In other processes, the zinc oxide is dissolved in a molten slag and is reduced directly from the slag.

If sulfides are used as feed materials, it is necessary to first remove the sulfur by roasting. Sintering is the usual roasting method used as it produces a hard, coarsely sized, or lump material, with a reasonably porous structure. This is required for high temperature gas reduction, where it is important to maintain an open porous mass within a furnace to minimise gas flow restrictions and to avoid dust carryover in product gases containing zinc vapour. Many different types of furnaces have been used to carry out the reduction process, ranging from sealed retorts to the blast furnace, electric furnaces and slag bath reactors.

It is not thermodynamically possible to directly produce liquid zinc under practical reduction conditions, as explained in Chapter 11. In all cases zinc is produced in vapour form by the reduction reactions, and is removed in an exit gas stream from which it may be condensed to liquid metal, or it may be re-oxidised to a zinc oxide fume. High temperatures are needed to achieve stable zinc vapour in the presence of carbon dioxide and water vapour. As gas mixtures are cooled, the equilibrium will shift back to re-formation of zinc oxide and CO. An appreciation of the thermodynamics involved is necessary to understand the basis of many of the processes used and is briefly covered in Chapter 11.

Zinc may be simply condensed by cooling gases containing zinc vapour where CO only is present, such as from a sealed retort where the reaction heat is supplied externally through the walls of the retort. In that case re-oxidation is not possible.

For processes that utilise the *in situ* combustion of carbon to provide reaction heat, such as the ISF, the zinc content of the gas is more dilute and the gases tend to contain high levels of CO₂ as well as H₂O. If the gas is simply cooled, zinc will be re-oxidised. To overcome this problem, use is made of methods to rapidly chill the gas stream and absorb or condense the zinc before a significant level of re-oxidation can occur. These methods rely on the fact that the reaction of CO₂ and Zn vapour is relatively slow. The condensation process itself is difficult and can be severely impacted by the presence of dusts and other volatile compounds in the gas stream. Halides in particular interfere with the condensation process.

In many processes, the conditions and properties of the reduction gas stream are unsuitable for condensation due to the presence of interfering materials. In that case, oxygen can be introduced and the zinc metal vapour can be oxidised to a fine particulate zinc oxide fume. This may be collected by filtration of the gas and can be used as feed to a further process for reduction to zinc metal. Most processes handling low-grade residues and secondary materials fall into this category. Such processes are classified as Fuming Processes and have been detailed in Chapter 16.

Metal produced by carbothermic reduction is heavily contaminated with lead and cadmium and must be refined. The principal methods of refining used are Liquation and Distillation. Liquation simply cools the zinc close to its freezing point, allowing dissolved metals such as lead and iron to be removed as separate phases. However, the product zinc retains some dissolved components, particularly where eutectics can form.

Distillation can separate zinc from most metals due to its relatively low boiling point and cadmium can be separated due to its even lower boiling point. Depending on how far the distillation is carried,

high purity metal can be produced by this method, but at a significant energy cost. Details of these procedures are given in Chapter 15.

Many of the carbothermic reduction processes reviewed are obsolete, such as retorting methods. The ISF remains as the primary pyrometallurgical method of zinc production. There is however perhaps more and growing interest in the use of these processes for the treatment of residues and secondary materials, particularly fuming processes involving the production of zinc oxide.

A listing of world zinc plants as at the year 2003, utilising pyrometallurgical reduction processes is given in Table 1.4.

TABLE 1.4

World primary pyrometallurgical zinc plants in 2003.

(Source: International Zinc Association, International Lead Zinc Study Group.)

Country and Company Name	Location	Process	Year first operated	Annual Capacity (tonnes)
EUROPE				
GERMANY Berzelius Metallhütten	Duisburg	ISF	1966	100 000
ITALY Eniressorse	Porto Vesme	ISF	1972	70 000
MACEDONIA Zopilnica	Titov Veles	ISF	1973	66 000
POLAND Miasteczko Slaskie	Miasteczko	ISF	1972	75 000
ROMANIA Sometra SA	Copsa Mica	ISF	1966	66 000
NORTH AMERICA				
USA Zinc Corporation of America	Monaca	ER	1930	160 000
ASIA				
JAPAN Hachinohe Smelting Co Sumiko ISP Co	Hachinohe Harima	ISF ISF	1969 1966	118 000 90 000
CHINA	Shaoguan 1 Shaoguan 2 Huludao Changsha	ISF ISF VR VR	1975 1996	75 000 75 000 210 000 12 000
INDIA Hindustan Zinc	Chanderiya	ISF	1991	70 000

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James, S E, Watson, J L and Peter, J, 2000. Zinc production – a survey of existing smelters and refineries, in *Proceedings Lead-Zinc 2000*, pp 205 –225 (TMS:Pittsburgh).

Historical Background

ZINC PRODUCTION IN EARLY TIMES

Zinc was not isolated as a separate metal in ancient times, although brass as an alloy of copper and zinc was known in Roman times. The alloy was produced by heating copper granules together with zinc oxide and charcoal in a sealed crucible. Zinc oxide was known and was collected as a fume from copper smelting operations.

The first evidence of zinc metal production appeared in India in the Middle Ages and also in China. The metal was used for coinage in China in the 15th century and was exported to Europe from India in the 17th century by Portuguese and Dutch traders. The unwrought metal was generally known as 'Tutenag' or 'Spelter'. Zinc was produced by retorting in earthenware cylinders packed with zinc oxide and charcoal, and heating in a slow fire. An extension of the cylinder, or retort, projected above the fire and provided a relatively cold surface on which the zinc could condense and collect.

Much of the early studies of zinc and its compounds related to alchemy with the view that calamine or zinc carbonate was an agent for the transformation of copper into gold. Zinc as a separate metal was collected from the walls of shaft furnaces used for the smelting of lead in the Hartz region of Germany, but was seen as related to bismuth, tin or silver and was not connected with spelter.

RETORT PROCESSES

The first record of an attempt to produce zinc metal commercially in Europe was a patent granted to William Champion of Bristol in 1738. The process involved retorting locally mined calamine ores with charcoal in a retort. Champion constructed an operation at Warmley near Bristol in 1743 and successfully produced zinc metal. The process was improved by Johann Ruberg who constructed a retort plant in 1798 at Wessola in Upper Silesia based on extensive calamine deposits in that region.

The process was further refined and extended by Abbe Dony in Liège as the forerunner to the horizontal retort and formed the basis of the Belgian zinc smelting industry which drew on the calamine deposits of the Aachen area.

During the 19th century, the zinc smelting industry developed largely in Germany and Belgium based on the horizontal retort and the local calamine deposits. The first commercial plants in the USA were built in 1860 at La Salle, Illinois and at South Bethlehem, Pennsylvania.

Initially production was based entirely on oxidised zinc ores, but as these deposits were depleted, attention turned to the use of sulfides or 'zinc blende', which required initial roasting to remove sulfur. The first patent covering the roasting of zinc blende was granted in 1758 but it was not until the development of the mechanically rabbled Hegelen Furnace in 1881 that roasting on a significant scale was practiced.

During the 19th century, improvements were made to the horizontal retort in terms of firing with gas, in zinc condensation efficiency and in the mechanisation of the filling and emptying of retorts. However, the process remained a batch operation until the successful development of the vertical retort by the New Jersey Zinc Company in 1925, after previous unsuccessful attempts in Germany and the UK.

Up to 1914, the zinc smelting industry was dominated by Belgium, Germany and the USA. Britain had largely neglected to develop its own industry and drew most of its supplies from Belgium and Germany. Those industries in turn sourced their raw materials largely from mines in Australia and the Americas. With the advent of the First World War, Britain had to draw supplies from the USA, which

saw a major expansion of its industry. There was also a major effort to invest in new zinc smelting operations with emphasis given to the new electrolytic process.

THE ELECTROLYTIC PROCESS

Until 1915, the traditional production of zinc metal relied entirely on pyrometallurgical processes utilising the relatively high vapour pressure of zinc metal and the ability to separate the metal by distillation. The horizontal retort process was well entrenched at that time, but was a batch operation with high-energy consumption, high labour requirements, and produced a relatively impure product. The electrolytic process had been applied to the recovery of copper and particularly to the refining of copper, as developed by Elkington in Birmingham between the years 1865 and 1870. Electrowinning of copper from low-grade ores had been successful and application of the electrolytic process to zinc had many similar attractions.

The roasting of zinc blende ores and leaching of zinc as zinc sulfate from the resulting calcines was practised in the 1880s to provide a feedstock for the production of lithopone (a mixture of zinc sulfide and barium sulfate), extensively used as a pigment at that time. Attempts were made to electrolyse the zinc sulfate solutions derived from this source but with little early success. A process that foreshadowed modern electrolytic practice was patented by L Letrange in Paris in 1881. The US Patent was granted in 1883. No details were provided on the need for solution purification and it would appear that such difficulties were unrecognised at that time and impeded the development of the electrolytic process using the sulfate system for around 30 years.

Development of an alternative chloride system had more early success and resulted in the construction of a plant in Furfurt, Germany in 1894. This plant was based on a process developed by Carl Hoepfner and produced zinc from the leaching of pyrite cinders from an associated sulfuric acid plant. By-product chlorine was used to make bleaching powder. Two more plants based on this process were constructed in Germany and one in England for Brunner Mond and Company in Winnington, which operated for 27 years from 1897 to 1924, producing zinc of 99.96 per cent purity. Englishman E A Ashcroft investigated both hydrometallurgical and molten salt chloride systems, and pilot operations were built at Cockle Creek in Australia in the mid 1880s based on the leaching of calcines with ferric chloride and electrolysis of the resulting zinc chloride solution. A small commercial zinc plant was constructed in 1896 based on Broken Hill ores but was not a commercial success.

The need to purify solutions for the sulfate process was recognised by a number of inventors in the period 1907 to 1914. Work by the Siemens and Halske company in Germany resulted in a number of patented techniques. The work of P C C Isherwood, U C Tainton, and A G French who developed techniques for electrolysis of zinc sulfate solutions containing manganese, all advanced the understanding of the technical requirements for solution purification and the electrowinning of zinc from sulfate solutions.

The advent of the First World War promoted active interest in the development of alternative zinc production operations with access to large resources located in the USA, Canada and Australia. Initial research and development work was largely undertaken by the Anaconda Copper Mining Company and the Consolidated Mining and Smelting Company of British Columbia (now Cominco). A pilot plant of 10 tpd capacity was built by the Anaconda Copper Mining Company at Anaconda, Montana in 1915 and was so successful that a 150 tonne per day plant was constructed shortly after at Great Falls, Montana. At Trail in British Columbia, the Consolidated Mining and Smelting Company built a small pilot operation in 1913, which was expanded to 35 tpd in 1915, and then rapidly expanded to 75 tpd. In Australia, Amalgamated Zinc (de Bavay's) Limited commenced investigations in 1915 on the production of zinc from the Broken Hill resource. Investigations were based on successful North American technology. The Electrolytic Zinc Company of Australasia was formed in 1916 to establish a plant at Risdon, Tasmania, based on low cost hydroelectric power, and a pilot facility was constructed

in the following year. A 10 tpd plant commenced operation in 1918 and was replaced by a 100 tpd operation in 1920.

Based on the assumption that the electrowinning of zinc was not practical from an acid solution, a process was developed in 1914 for treatment of ores from the Bully Hill Mine in Shasta County, California. Zinc was precipitated as hydroxide from zinc sulfate leach solutions using lime and was then added directly to the electrowinning cells to neutralise acid as it formed at the anode. Although good quality zinc cathodes were produced, the process consumed large quantities of sulfuric acid and was not competitive with the alternative acid electrolyte process.

A significant number of other experimental or small commercial plants were built in North America, Europe and Japan in the period to 1920. However, the three major operations at that time (Great Falls, Montana; Trail, British Columbia; and Risdon, Tasmania) continued in operation and pioneered many of the basic features of the electrolytic zinc process. These developments included the use of lead anodes, the use of aluminium cathodes, purification requirements and methods, and an understanding of the fundamental aspects of the electrowinning of zinc. Although the principles of the process have remained unchanged since 1920, there have been a number of significant improvements. The first was the reduction in the lead content of cathode zinc from 0.03 per cent to less than 0.01 per cent through the use of lead anodes containing silver to reduce its corrosion. This was developed by U C Tainton at the Bunker Hill, Idaho plant and followed the need for higher purity zinc for the manufacture of diecasting alloys, which were subject to intergranular corrosion if the lead content exceeded 0.01 per cent. Anodes containing 0.5 per cent silver are now normally used together with the addition of strontium carbonate to the electrolyte to further lower lead levels in solution by ion exchange with precipitated strontium sulfate in suspension in the electrolyte.

RECOVERY OF ZINC FROM LEACH RESIDUES

The second significant advance in the electrolytic zinc process was the development of methods to process ferrite leach residues. Any iron present in zinc concentrates combines with zinc oxide during roasting to form a zinc ferrite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$). This material is not dissolved during normal dilute acid leaching at temperatures up to 60°C. Consequently, most of the associated zinc is locked into the leach residue, resulting in zinc recoveries for the total process generally between 85 per cent and 90 per cent, but dependent on the iron content of the concentrate. Ferrite residues were treated by two principal methods - the Waelz process and by feeding to a lead smelter. The latter approach was only useful if the residue contained reasonable quantities of lead and silver, in that case zinc may be recovered by fuming from the lead blast furnace slag for return to the zinc plant as zinc oxide.

The Waelz process, which involves the fuming of zinc from the residue in a rotary kiln, was applied primarily to recover zinc but also recovered lead and some silver into the zinc oxide fume. However, it was a substantial consumer of coke or high rank coal.

The zinc recovered by these processes was high cost, therefore a more efficient and economical means of extracting zinc from ferrite residues was sought. It had been known since the 1930s that the zinc and iron contents of ferrite residue could be leached in hot sulfuric acid solutions (above 90°C and above 120 g/L H_2SO_4), but the problem had been to devise a means of precipitating iron in a form which could be readily settled, filtered and washed without entraining excessive amounts of zinc. Separation of large amounts of iron as ferric hydroxide by precipitation with zinc oxide was quite impractical in this regard. During the 1960s, efforts were concentrated on the precipitation of iron as a crystalline basic ferric sulfate and it was found that compounds of the form of the mineral 'jarosite' ($\text{Na}_2\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12}$) could be formed at temperatures above 90°C. This led to the development of the jarosite process in which ammonium jarosite was commonly employed as the means of precipitating iron. The process was simultaneously developed by the Electrolytic Zinc Company of Australasia, the Det Norske Zink Co in Norway, and Asturiana de Zink SA in Spain, and was widely and rapidly applied throughout the

industry in the late 1960s and early 1970s. The result of this innovation was the improvement of zinc recovery from as low as 85 per cent to at least 95 per cent and up to 97 per cent. Many improvements and variations of the jarosite process have subsequently been made, such as the 'conversion process' developed by Outokumpu Oy in which the leaching of ferrites and precipitation of jarosite take place simultaneously in the same stage.

At almost the same time as the development of the jarosite process an alternative, but similar approach to iron precipitation was developed by Vieille Montagne SA at the Balen plant in Belgium, which involved the separation of iron in the form of the mineral 'goethite' ($\text{FeO} \cdot \text{OH}$). This required similar conditions to jarosite and produced a material of higher iron content than jarosite but also of higher zinc content, and did not achieve an overall zinc recovery as high as the jarosite process.

As an extension, the precipitation of iron at elevated temperature and pressure in an autoclave as hematite was also developed and implemented at one plant in Germany and one in Japan. Although this process had aims of disposing of the hematite as a feedstock for iron production, it was not of sufficient purity and this method of disposal did not eventuate.

Because of the environmental difficulties with the disposal of iron residues such as jarosite, there are growing pressures for the development of alternative approaches or methods of additional residue processing to improve environmental acceptability.

DIRECT LEACHING OF ZINC CONCENTRATES

The third significant process improvement was the development of procedures for the direct leaching of zinc from sulfide concentrates, avoiding the operations of roasting and sulfuric acid production. This was originally developed as a pressure leaching process by Sherritt Gordon Ltd and was first applied at Cominco's Trail plant in 1982. A number of installations have been built since. All are subsidiary operations to roast-leach operations except for the Flin Flon, Manitoba plant of the Hudson Bay Mining and Smelting Company which has been converted entirely from roast-leach to a two stage pressure leach. Although more complex, the incentive for this change was the ability to produce sulfur in elemental form rather than as sulfur dioxide or sulfuric acid, for which disposal was a problem at the remote location.

The more recent development of atmospheric pressure direct leaching methods using ferric iron as an oxygen carrier, is a major advance and has been implemented at a number of plants during the 1990s as a supplement to roast-leach operations (Union Minière (Umicor) at Balen, Outokumpu at Kokkola, and Korea Zinc at Onsan).

EVOLUTIONARY DEVELOPMENTS

Apart from the significant process changes mentioned above, there have been many evolutionary improvements in the design and operation of the electrolytic zinc process, including circulating electrolyte cell house designs, larger electrodes and fully mechanised and automated electrode handling. Roasting equipment has also undergone marked change from early rabbled hearth roasters, to suspension roasters, and finally to fluid bed roasters. Leaching and purification has changed from batch to continuous operations with vastly improved material handling equipment, settling and filtration equipment, and automated control and instrumentation.

Attempts have been made to introduce solvent extraction-electrowin methods for zinc, as for copper, but with limited success due to the fact that highly selective solvents for zinc have not been developed, as is the case with copper. It is possible in circumstances where there are high levels of particular impurities to apply solvent extraction methods, and this has been used by the Spanish technology group Técnicas Reunidas in the Skorpion Zinc Project in Namibia. However, large scale applications cannot be foreseen at the time of writing.

The electrolytic zinc process has been greatly refined since its beginnings in 1915, replacing the retort process and representing close to 80 per cent of world zinc production by the end of the 20th century.

IMPERIAL SMELTING PROCESS

Apart from the impetus to progress the electrolytic process, the First World War compelled Britain to give attention to its own zinc smelting industry and the government sponsored National Smelting Company was formed in 1917 to acquire existing operations at Swansea and elsewhere and to construct a new smelter at Avonmouth near Bristol. Because of the high cost of operating horizontal retorts, research was initiated into new methods of zinc production for use in the expanded British smelting industry. The electrolytic process was not favoured because of the relatively high cost of electric power and a new process based on carbothermic reduction was sought. This led to the concept of the zinc blast furnace.

The National Smelting Company was incorporated into the Imperial Smelting Corporation in 1929 formed by an amalgamation of British smelting interests and Australian mines through The Zinc Corporation. The decision was then made to apply the new technology developed by the New Jersey Zinc Company and a vertical retort plant was constructed at Avonmouth and completed in 1934. Development on the blast furnace concept was slow until the impetus of the Second World War resulted in the commencement of experimental work in 1938 and the first pilot furnace in 1943. Problems with zinc condensation led to the development of the lead splash condenser and construction of the first integrated development furnace in 1950. Additional development furnaces were built and the first commercial operation was completed at Swansea in 1960, followed immediately by a unit at Cockle Creek (Australia) in 1962. Subsequently a number of plants were constructed around the world to replace old retort plants and in fact supplanted any further construction of retort plants. The blast furnace-condenser system was named the Imperial Smelting Furnace (ISF), and the overall process the Imperial Smelting Process (ISP).

Zinc produced by the retort processes was suitable for galvanising steel by the hot dip method and for the production of zinc chemicals but was too impure for the preparation of zinc alloys. Following its pioneering efforts in the development of zinc based diecasting alloys in the late 1920s, the New Jersey Zinc Company set out to develop a refining technology for zinc derived from retort processes. This resulted in the reflux distillation column and the New Jersey Column Refining Process, which was implemented in 1930. This technology was also adopted by Imperial Smelting and became an integral part of an ISP plant.

By the late 1960s and early 1970s the old horizontal retort plants had almost been fully replaced. There was competition at that time between the electrolytic process and the Imperial Smelting Process, with both processes using similar high-grade concentrates. The advantage of the ISF was the ability to simultaneously produce lead bullion and recover precious metals directly into that bullion, but gradually the electrolytic process gained predominance because of the superior quality of its product and in the longer term because of its higher efficiency and lower overall cost structure. Zinc from the ISF required refining to compete, and this operation was a significant added cost and complication. This deficiency was exacerbated by the change away from batch steel sheet galvanising to continuous galvanising, and the corresponding change in the specification of zinc required for the galvanising bath to low levels of contained lead.

At the beginning of the 21st century the electrolytic process is dominant and the Imperial Smelting Process is being phased out as a primary smelter with a role progressively seen as a means of processing secondary materials. Another factor which possibly contributed to the decline of the Imperial Smelting Process was the improvement in mineral dressing over the period from 1960, leading to the improved separation of zinc and lead into high grade concentrates. This reduced the availability of mixed bulk

concentrates and reduced the attraction of a process able to simultaneously produce both zinc and lead metal, albeit in a relatively impure form.

The rise in availability of secondary zinc materials such as electric arc furnace dusts from the processing of scrap steel, coupled with the increasing cost of disposal as earth fill due to environmental regulations, provided incentive for the development of a range of new smelting technologies during the 1990s. Many of these technologies involved electric furnace reduction coupled with direct condensation to zinc metal. However, most processes failed due to technical difficulties and inefficiencies. The major method of handling these materials remained as fuming using the Waelz kiln process. Other methods of zinc fuming have also been developed and provide zinc oxide feed to either the ISF or electrolytic processes for zinc metal production.

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Raw Materials

BACKGROUND

Early production of zinc metal in China and India and indeed in Europe in the 18th century using retorting methods was based on non-sulfide or oxidised ores with the principal source being ‘Calamine’ or zinc carbonate. There was early confusion in relation to zinc mineralogy and although sulfides were recognised as a possible source for zinc production in a UK patent by William Champion in 1738, it was not until the middle of the 19th century that zinc sulfide or ‘Blende’ was used as smelter feed. The term ‘Blende’ derived from ‘blenden’ meaning to blind or obscure arose in Germany to describe a form of mineralisation similar in appearance to galena but which did not produce lead or silver when smelted. The discrete zinc sulfide mineral was also termed sphalerite by the early lead smelting industry, which comes from the Greek word meaning ‘treacherous’ for the same reasons.

Early zinc production was centred on regions where large deposits of calamine existed, such as the Mendip Hills near Bristol in the UK, the large Aachen deposits, which supplied the Belgian smelting industry, and the deposits in Upper Silesia. Calamine deposits were largely worked out in the late part of the 19th century and the use of Blende became the principal source of zinc for the growing zinc smelting industry.

Sulfide mineralisation is normally a mixture of many metal sulfides but often has a strong association with iron as pyrite or pyrrhotite, and also with lead as galena and with copper. Early separation techniques relied on size reduction and gravity separation methods, which were reasonably successful for lead separation due to the high specific gravity (SG) difference, but were generally inadequate for the separation of sphalerite with an SG of 4.0. This difficulty became acute with the discovery of large zinc resources such as the Broken Hill field in Australia and provided incentive for the development of the froth flotation process for differential mineral separation. Zinc sulfide concentrates are the major raw material for the zinc smelting industry today.

ZINC MINERALOGY

The common zinc minerals are given in Table 3.1.

All Periodic Table Classification Group IIB elements will be strongly associated and hence zinc mineralisation always contains cadmium and mercury. The mean ratio of zinc to cadmium is around 300:1 but can vary considerably. The level of mercury shows a much greater variation with zinc to mercury ratios averaging 15 000:1.

TABLE 3.1
Common zinc minerals.

Mineral	Formula	Zinc content %
Sphalerite, Zinc Blende or Wurtzite	ZnS	67.1
Marmatite (iron in solid solution)	(Zn,Fe)S	< 67.0
Smithsonite or ‘Calamine’	ZnCO ₃	52.2
Hydrozincite	3ZnO.2ZnCO ₃ .3H ₂ O	59.5
Willemite	2ZnO.SiO ₂	58.7
Hemimorphite	4ZnO.2SiO ₂ .2H ₂ O	54.3
Zincite	ZnO	80.4

Note: Hemimorphite was also termed ‘Calamine’ in North America.

The sphalerite contained in zinc concentrates normally contains some iron in solid solution. In the extreme, the iron content can be up to 20 per cent as FeS and generally when above ten per cent the mineral is termed Marmatite. The iron so contained within the sphalerite crystal lattice is termed 'marmatitic iron'. Such iron can also be replaced by manganese.

In most occurrences sphalerite is accompanied by galena in varying amounts. Pyrite (FeS₂) is also a most common association and can often represent the main mass of the sulfide orebody. Pyrrhotite (FeS) occurs to a lesser extent as well as chalcopyrite (CuFeS₂). Silver mineralisation is also common but often in the form of complex minerals such as tetrahedrite ((Cu,Fe)₁₂Sb₄S₁₃) in which the copper is part replaced by silver. Silver can occur in solid solution in sphalerite and pyrite as well as in other complex minerals.

Common minor or trace element associations with sphalerite are arsenic, antimony, germanium, thallium, indium, selenium, cobalt and nickel. Common gangue minerals are quartz, calcite (CaCO₃), dolomite (MgCO₃), fluor spar (CaF₂), barite (BaSO₄), rhodochrosite (MnCO₃) and rhodonite (MnO.SiO₂).

SEPARATION AND CONCENTRATION OF SULFIDE ORES

Most commercially viable zinc orebodies contain zinc above four per cent and rarely above 20 per cent in mass, although zones of pure sphalerite can occur. Zinc sulfide mineralisation must be separated from gangue and other metallic sulfides, and must be concentrated to a degree suitable for acceptance by the smelting operation. The degree of separation and concentration required is dictated by both economics and competitive pressures. One aim is to minimise the amount of waste materials associated with the zinc mineralisation so as to reduce the costs of smelting and waste disposal requirements by the smelter, as well as to reduce the costs of transport of the concentrate from the mine to the smelter. It is preferable to retain as much waste in mine tailings as possible.

There are competitive pressures on mining operations to produce concentrates that do not depart significantly from generally accepted specifications. Otherwise specialised smelting practices will be required which tie the mine and smelter. This may be appropriate for integrated mine - smelter operations where the mine resource is large and can supply the smelter for a long period. But generally this does not represent the bulk of the industry, which relies on traded zinc concentrates and where flexibility in feed sources is required. As a consequence, the specification range of zinc concentrates is relatively narrow and mine separation processes must meet these specifications to support an economically viable operation. As feed to an electrolytic zinc smelter, the broad concentrate specification is as given in Table 3.2.

The characteristics of zinc ores vary widely and are often complex assemblies of mineralisation. Each deposit is more or less unique and requires individual tailoring of the separation process and reagents used to optimise separation efficiency.

Separation and concentration involves two main steps:

1. size reduction of the ore so that the individual mineral grains are liberated and separated from one another.
2. selective physiochemical separation of the individual mineral grains by froth flotation to form separate metal concentrates.

Size reduction for mineral grain liberation involves crushing and grinding to an 80 per cent passing size of less than 50 microns and for particularly complex fine grained ores to less than ten microns. Fine

TABLE 3.2

Typical zinc concentrate target specifications.

Element	Composition range %
Zn	47 to 56 %
Fe	< 10 %
Pb	< 3 %
Cu	< 2 %
S	30 to 32 %

grinding is a high cost in both equipment and energy and there have been developments to improve the efficiency of this operation, such as tower and stir mills.

Primary crushing may reduce 'as mined ore' to less than 200 mm which is then, in the conventional approach, reduced in secondary and tertiary crushers followed by rod and ball mill grinding to the required particle size. Final sizing classification is usually achieved by operating the ball mill in closed circuit with hydrocyclones.

If the ore is suitable, autogenous grinding may be used in which large lump ore is added directly to a large tumbling mill. This replaces conventional secondary and tertiary crushing, rod and possibly ball mills, saving on the cost of steel grinding media, which can be consumed at a rate of around 1 to 2 kg/tonne of ore. The low SG of lump ore in comparison with steel balls requires a much larger diameter mill to achieve the same grinding forces. Full autogenous grinding is often difficult to achieve if the ore tends to fracture and break down readily on a macro scale. However, in this case some steel balls can be added to give semi-autogenous operation and greatly extend the application of this approach, to the point where this has largely replaced the conventional multi stage size reduction.

For fine grinding, additional ball mill capacity is necessary. If very fine grinding is required then tower or stir mills have been developed to significantly reduce energy costs. In this type of equipment grinding of the mineral pulp occurs within an agitated bed of coarse gravel. The bed may be agitated by circulation using a screw or by slow moving paddle mixers. These mills have significantly lower specific energy consumption, which is critical for size reductions to ten microns or less. Often fine grinding can be applied part way through the separation process rather than on total ore feed and after separation of a large part of the gangue minerals. This reduces the quantity of material subjected to fine grinding and hence minimises overall grinding costs.

Physical separation of minerals generally relies on the use of froth flotation. Flotation is based on the following principles:

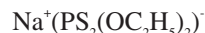
- Sulfide minerals may be conditioned by the addition of surface active chemicals to cause them to become water repellent or hydrophobic.
- The collisions between mineral particles with hydrophobic surfaces and bubbles of air within the mineral pulp will result in the attachment of the mineral particle to the air bubble.
- Mineral particles that remain wetted (hydrophilic) will not attach to the air bubbles.
- Reagents are used to produce a froth of reasonable stability to allow its collection and separation from the surface of the mineral pulp.

Flotation equipment consists of a series of agitated tanks through which the mineral pulp flows and into which air is dispersed as a stream of fine bubbles. A froth is formed on the surface containing the hydrophobic mineral particles and is skimmed off into a trough where it collapses and flows into a collection tank.

It is a relatively simple matter to bulk float all sulfide minerals by the addition of surface active chemicals known as collectors. These materials are usually an organic molecule containing a sulfur bearing group at the polarised end which can bond with the sulfide mineral forming an attached organic and hydrophilic surface layer. The most common collectors are:

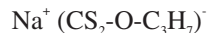
Dithiophosphates such as:

Sodium diethyl dithiophosphate



Xanthates such as:

Sodium isopropyl xanthate



Differential flotation can be achieved when only specific minerals are floated. This is done by the use of additives to the pulp to depress or promote the collection of particular mineral surfaces. The particular response of minerals contained in an ore will differ widely and hence there is a considerable variation in flotation practices from one plant to another. But the general approach is to first float copper and depress the other base metal sulfides, then float lead and finally zinc. The aim is generally to depress pyrite, but this can be difficult and it is often the major diluent in zinc concentrates.

The pH of the pulp is an important depressant showing selectivity for individual minerals and depression in the following order as pH is raised:

- sphalerite (ZnS),
- pyrrhotite (FeS),
- galena (PbS),
- pyrite (FeS₂),
- chalcopyrite (CuFeS₂),
- sphalerite activated with copper sulfate, and
- tetrahedrite ((CuFe)₁₂Sb₄S₁₃) for silver mineralisation).

Other depressants that have been used are zinc sulfate for sphalerite and cyanide for sphalerite and pyrite, although CMCs (carboxy methyl cellulose-dextrose or starch derivatives) tend to be more commonly used at the present time.

Following depression of most of the sulfide mineralisation and flotation of lead and copper, copper sulfate is generally added to promote the flotation of sphalerite. In simplistic terms this reacts with the zinc sulfide surface to form a copper sulfide layer, which will readily respond to the collector. The action of cyanide as a depressant is partly due to its ability to complex copper ions in solution and prevent any such activation.

The kinetics of the flotation process is an important factor and some of the relative reaction rates may be quite different, allowing some opportunity for differentiation by this means and placing emphasis on the importance of process residence times. Other factors of importance in control of the process are the pulp density, pulp temperature, aeration rates and bubble size.

A sample copper - lead - zinc separation flow sheet is shown in Figure 3.1.

There are many different flow sheets used for the handling of particular ores, however a typical flow sheet usually involves an initial flotation stage or 'rougher circuit', the crude concentrate from which is re-floated in a 'cleaner circuit' for upgrading. The tailings from the 'rougher circuit' are also re-floated in a 'scavenger circuit' to recover any residual mineral values. A multiplicity of such stages and the recycling of intermediate streams can lead to a highly complex flow sheet with a high level of internal recycle and difficult control problems.

The basic aim is to optimise the grade of the concentrate produced and the recovery of valuable metals into their respective concentrates. This may be expressed as a grade - recovery curve for a particular ore as illustrated in Figure 3.2. The position of the curve is to some extent a function of the flow sheet used, but is critically dependent on the grind size. Finer grinding will improve minerals liberation, but the recovery of very fine particles can be reduced due in large part to their inability to collide with and attach to air bubbles. This phenomenon has been termed 'sliming' and is a common problem for galena flotation, which is prone to ready fragmentation into ultra fine particles. Specialised flotation cells to generate fine bubbles can improve this situation.

The particular position on the grade-recovery curve for flotation plant operation is dictated by competitive pressures for sale of the concentrate and overall economics of the mining operation, including transportation issues. It is a complex balance, and many variables together with the total

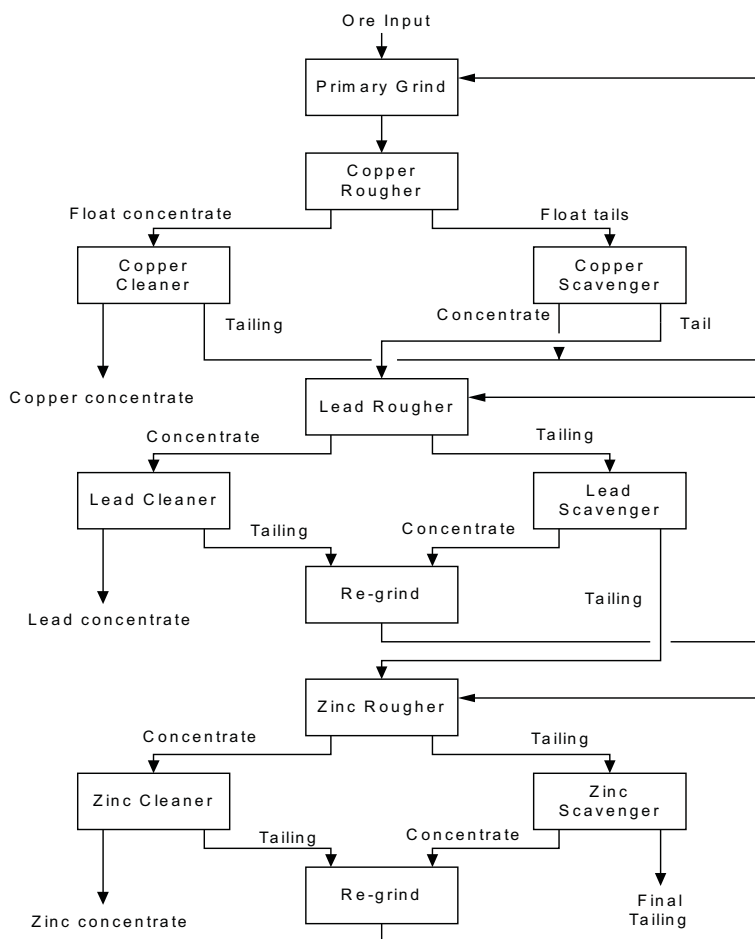


FIG 3.1 - Typical flotation flow sheet for Cu/ Pb/ Zn ore.

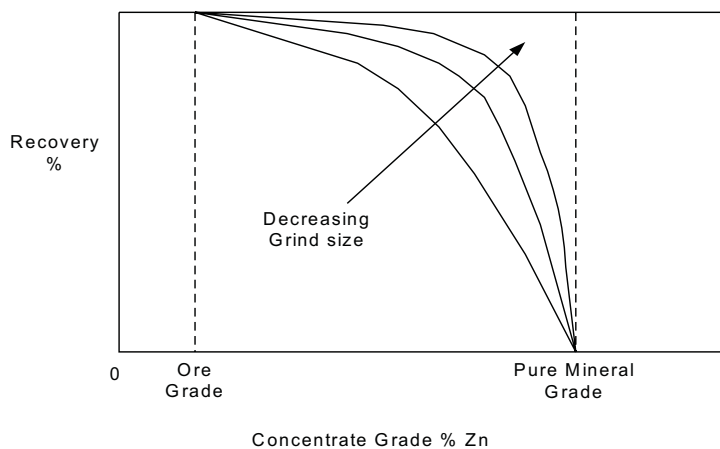


FIG 3.2 - Concentrate grade – recovery relationship.

mineral value recovered from the ore must be considered in order to select the optimum set of operating conditions. This involves consideration of all primary and by-product concentrates produced.

In some instances it is impractical to grind fine enough to achieve satisfactory separation and resort is made to the production of a bulk or middling concentrate containing high levels of two or more valuable metals at relatively high recovery. This can be a suitable feed to an Imperial Smelting Furnace, but is not suitable as feed to an electrolytic smelter. In such circumstances it is possible to produce part of the zinc and lead content of the ore as high grade concentrates and part as a bulk or middling concentrate to maximise recovery. The economics of the mining operation are largely determined by the head grade of the ore and the metal recovery achieved into commercially acceptable concentrates.

COMMERCIAL ZINC CONCENTRATES

Although the zinc sulfide concentrates produced by the above processes have individual characteristics that must be carefully assessed by the smelter, they are largely treated as a commodity with compositions falling within common and accepted ranges and limits.

Electrolytic zinc plants represented over 85 per cent of world zinc production in 2003 and hence their requirements largely set the specifications for zinc concentrates. The average composition range for traded zinc concentrates is given in Table 3.3, which also shows the maximum limits commonly preferred.

TABLE 3.3
Commercial zinc concentrate specifications.

Element	Normal Range	Preferred Maximum Limits
Zinc	48 to 56 %	
Lead	1.0 to 3.0 %	3.5 %
Cadmium	0.15 to 0.30%	
Copper	0.10 to 1.5 %	2.0 %
Iron	1.5 to 10 %	12 %
Sulfur	30.5 to 32.5 %	
Magnesium	0.05 to 0.2 %	0.3 %
Silica	0.2 to 2.5 %	3.0 %
Calcium	0.2 to 1.0 %	2.0 %
Manganese	0.02 to 0.8 %	0.4 %
Arsenic	0.01 to 0.5 %	0.5 %
Antimony	0.01 to 0.1 %	0.2 %
Sodium	0 to 0.2 %	0.01 %
Potassium	0 to 0.1 %	0.01 %
Silver	10 to 200 g/t	
Gold	0 to 2 g/t	
Nickel	10 to 100 g/t	100 g/t
Cobalt	10 to 200 g/t	200 g/t
Mercury	10 to 100 g/t	60 g/t
Thallium	0 to 50 g/t	50 g/t
Indium	5 to 500 g/t	
Germanium	0 to 100 g/t	40 g/t
Gallium	0 to 200 g/t	
Selenium	0 to 50 g/t	50 g/t

Barium	100 to 500 g/t	
Bismuth	10 to 500 g/t	
Fluorine	0 to 200 g/t	100 g/t
Chlorine	10 to 1000 g/t	500 g/t
Carbon	0 to 1000 g/t	1.0 %

A range of impurity elements need to be separated in the electrolytic process and if in excess of the normal capabilities of the process, cost penalties may be applied. Alternatively the material may be unacceptable or is only accepted in limited amounts as part of a feed blend. Common penalty elements and limits are as follows:

Iron	8 to 10%
Magnesium	0.3%
Arsenic	1000 g/t
Antimony	1000 g/t
Mercury	100 g/t
Nickel	100 g/t
Germanium	50 g/t

Some additional elements, which may not commonly be present in excessive amounts, can also attract a penalty. Carbon is such an example since in excess it imposes a significant heat load on the roasting operation, which may restrict the throughput of concentrates. Carbon is likely to attract penalties over one per cent.

Other elements may simply not be manageable in excessive amounts and will limit the quantity that can be accepted in feed to the smelter or will be completely rejected. Such elements are:

Lead	- over 3 or 4 %
Silica	- over 3 or 4 %
Copper	- over 2 %
Manganese	- over 0.4 %

With the provision of feed to the Imperial Smelting Process the above constraints can be relaxed. There are no limits on lead content, and copper can be significantly higher. However, there can be penalties on silica, arsenic, bismuth and antimony, and many constraints are similar to those applied to lead concentrates since they relate to issues involved with the refining of by-product lead bullion.

Precious metals (silver and gold) are directly recovered into lead bullion with the Imperial Smelting Process, but report to complex low-value residues in the electrolytic process. This influences the ability to pay for precious metals within the zinc concentrates as feed to the electrolytic process.

COMMERCIAL TERMS FOR PURCHASE OF STANDARD ZINC CONCENTRATES

The structure of the terms formula on which the price of zinc concentrates is determined is essentially based on payment for 85 per cent of the zinc content of the concentrate at the prevailing zinc price less a treatment charge.

The formula originated in the early part of the 20th century when zinc was mostly produced by the horizontal retort process and metal recoveries were limited to around 85 per cent. In addition, the early electrolytic plants did not achieve much greater recovery due to their inability to extract zinc from zinc ferrite formed during roasting. Except for those plants processing low iron concentrates, it was not until the development of the jarosite and goethite processes in the late 1960s that the average electrolytic process lifted zinc extraction to 95 per cent or above. However, the terms remain unchanged with a

basic metal payment of 85 per cent of the zinc content, but with a qualifying minimum free metal allowance of eight units in the original concentrate. Hence the metal payment may be expressed as payment for the zinc content less eight percentage units or 85 per cent of the contained zinc, whichever is the lesser. Examples of metal payments are given in Table 3.4.

TABLE 3.4
Zinc concentrate metal payments.

Concentrate zinc content %	Zinc content paid for %	Zinc content as free metal to smelter %	Per cent of zinc content paid for
46	38	8	82.6 %
48	40	8	83.3 %
50	42	8	84.0 %
52	44	8	84.6 %
54	45.9	8.1	85.0 %
56	47.6	8.4	85.0 %

At the lower grades the above formulation to some degree reflects that the losses in metal from the smelter are governed by the quantity of residues and hence are proportional to concentrate input irrespective of its zinc content. For higher grades a fixed recovery is assumed.

Since zinc losses are now generally much lower than the terms allowance, the ‘free metal’ or unpaid zinc content represents a significant addition to the smelters financial return but is recognised in negotiation of the treatment charge which is usually lower than the actual cost of smelter operation.

The only other metal commonly paid for in zinc concentrates is silver and usually only above a base level of three troy ounces per metric tonne (or 90 to 100 grams). Normally only 75 per cent of the silver content above the base line is paid for which reflects the normal level of silver recoverable into a lead – silver residue.

The concentrate terms cover the payment for metal content as above at prevailing metal market prices such as the London Metal Exchange (LME) price for Special High Grade (SHG) zinc, less a treatment charge which is a fixed amount per tonne of concentrate. The treatment charge is the main negotiable item and is usually partly linked to the LME zinc price, being set at a nominated price and inflated or deflated by nominated fractions of the movement in the zinc price – generally within the range of eight to 15 per cent, and typically 12 per cent. The inflator is usually 50 per cent greater than the deflator. In times of surplus concentrate supply the negotiated treatment charges will tend to be high, favouring the purchaser, whereas in times of concentrate shortage the treatment charge will tend to be low, favouring the seller. Over an extended period the treatment charge expressed as a percentage of the concentrate zinc payment has averaged 40 per cent with a range of 32 per cent to 48 per cent.

For a typical zinc concentrate of 52 per cent zinc content and an LME zinc price of US\$1000 per tonne, the metal payment per tonne of concentrate will be (52 per cent to eight per cent) x 1000 = US\$440. The treatment charge will average around US\$180 per tonne of concentrate.

The concentrate value is therefore (440 – 180) = US\$260 per tonne.

The smelter return is the value of metal sold less the cost of the purchased concentrate. At 97 per cent zinc recovery the value of metal sold is 52 per cent x 97 per cent x 1000 = US\$504 per tonne of concentrates used. The smelter return is therefore US\$(504 – 260) = US\$244 per tonne of concentrate used or US\$484 per tonne of zinc recovered, which must cover the operating costs and profit of the smelter. This can also be regarded as composed of the treatment charge of US\$180 and the return from free metal recovered of US\$64 per tonne of concentrate. Close to one quarter of the smelter return comes from free metal and the remainder from the treatment charge. Since the treatment charge is

largely fixed, the metal pricing risk for the smelter is limited. On the other hand the concentrate supplier carries a much higher sensitivity to metal price movements, and under typical terms the concentrate supplier will receive 60 per cent of the increase in contained zinc value due to zinc price changes. Whereas the smelter will receive 37 per cent leaving three per cent as zinc lost in smelter residues for a smelter zinc recovery of 97 per cent.

Smelter revenues are boosted by an ability to recover and sell by-products such as sulfuric acid, cadmium, copper, lead and silver residues, as well as some minor elements such as cobalt and nickel, mercury, selenium, indium and germanium. Some valuable minor elements such as precious metals silver and gold can attract metal payments if present in excess of minimum specified amounts. For gold the payment can be 90 per cent of the content over 2.5 g/t and for silver the payment can be 75 per cent of the content over 90 g/t. However for most minor elements the by-product revenues are often less than the cost of separation, and in many cases the production of a by-product does provide an outlet for what might otherwise be a difficult disposal problem. In those cases excessive amounts over defined limits may attract a penalty to cover separation costs.

Pricing of concentrates for delivery on a particular date is based on average daily LME metal prices over a defined period ('The Quotational Period') and usually is set as the month following the month of delivery. This is intended to provide a close match with the timing of consumption of the concentrate and delivery of product metal. Otherwise there can be serious discrepancies and variations in pricing of the metal contained in the concentrates used and the pricing of the metal recovered and sold from those concentrates.

COMMERCIAL TERMS FOR THE PURCHASE OF BULK CONCENTRATES

The Imperial Smelting Process produces both zinc and lead, and can blend standard zinc concentrates with lead concentrates or preferably can use mixed bulk concentrates. Since the terms for low grade and mixed bulk concentrates are more favourable to the smelter due to the greater percentage of 'free metal', it is in the interests of an ISF smelter to source as much of its raw material as possible as bulk concentrates. The metal output of the plant will be reduced as more lower grade materials are processed due to the increased formation of slag, the associated losses of zinc in that slag, and the fuel utilisation to heat and melt the slag. Hence, there is a balance between lower cost raw materials and lower zinc production, which leads to an optimum grade of mixed feed. The best option is possibly the total use of bulk feed of relatively high grade in terms of total zinc plus lead content.

The terms for mixed bulk concentrates represent a mix between standard zinc and lead concentrate terms and the following is a typical example:

- zinc payment for the balance of the zinc content after deduction of 7.5 units at the LME zinc price for SHG zinc metal;
- lead payment for the balance of the lead content after deduction of 3 units at the LME lead price;
- silver payment for 90 per cent of the balance after deduction of 90 g per tonne of concentrate; and
- gold payment for 60 per cent of the balance after deduction of 2 g per tonne of concentrate.

The treatment charge is commonly US\$10 to US\$15 above the ruling treatment charge for standard zinc concentrates as given above, but with the price escalator three per cent lower at around nine per cent.

By way of example, and in comparison with standard terms above for standard zinc concentrates, a bulk concentrate of 45 per cent Zn and 15 per cent Pb content (ignoring silver and gold contents) and at metal prices of US\$1000/t for SHG zinc and US\$550/t for refined lead, the following will apply per tonne of concentrate:

Metal payments	Zinc (45% - 7.5%) x 1000 = US\$375/t Lead (15% - 3%) x 550 = US\$66/t
Treatment charge	US\$(180 + 15) = US\$195/t
Concentrate value	= 375 + 66 – 195 = US\$246/t

Allowing for 90 per cent lead recovery to bullion and for freight to a refinery and refining charges, the by-product value of lead bullion is worth US\$51/t of concentrate, and the net concentrate cost for zinc alone is US\$195/t of concentrate. Or US\$471/t of zinc recovered (92 per cent), which is significantly lower than the cost of US\$260/t for standard zinc concentrates, as given above, and equivalent to US\$515/t of zinc recovered.

SECONDARY MATERIALS

For secondary materials, including zinc oxide fume, acceptance by the smelter depends on a number of factors, the most significant being:

- The impact of displacement of standard concentrate feeds on by-product revenues such as sulfuric acid, and associated costs.
- The impurity content and capacity to handle an added impurity load. This particularly applies to halides contained in fume products.
- The capacity constraints within the smelter and whether the processing of non-standard feeds will increase or decrease zinc metal output.
- The impact on overall zinc recovery.

Because of these factors, the terms offered may vary widely from one smelter to another depending on the associated benefits and penalties, but in the event that these factors are minimal, a common guide to payment terms for high grade fume is of the order of 50 per cent of the contained zinc value at the prevailing LME zinc price. Otherwise, standard concentrate terms can be applied with adjusted treatment charges.

For low-grade residues and materials such as Electric Arc Furnace (EAF) dusts there are no standard terms. Acceptance by the smelter and the terms offered will depend entirely on related handling and processing costs as well as prevailing circumstances. It may be that a charge is levied for treatment with no metal payments, and this is indeed common for EAF dusts which otherwise must bear a significant disposal cost, since they contain the heavy metals lead and cadmium as well as zinc.

PART B

THE ELECTROLYTIC PROCESS

This part of the text covers hydrometallurgical methods of zinc extraction and the main steps in the Electrolytic Process using the sulphate system as the predominant method of zinc metal production. Other electrolyte systems and techniques are also covered.

Chapter 4	Roasting
Chapter 5	Leaching and Solution Preparation
Chapter 6	Solution Purification
Chapter 7	Electrolysis
Chapter 8	Melting and Casting
Chapter 9	Material Balance Control and Effluent Treatment
Chapter 10	Other Hydrometallurgical Systems

Roasting

PURPOSE

Early production of zinc was from oxide ores, and extraction processes were largely developed on the basis of direct reduction of oxidised feed materials. These materials were quite limited and the advent of sulfide ore extraction following development of the flotation process for mineral separation, greatly expanded the availability of zinc raw materials. This change in feed materials then required the conversion of sulfides into oxides as a preparatory stage to the application of known and established zinc extraction processes. This was done, in the first instance, by heap roasting with air, with the objective of eliminating all sulfur from the resulting oxides or calcine. Open heap roasting was not only relatively inefficient, but was clearly not environmentally acceptable and a parallel objective became the efficient capture and utilisation of the sulfur dioxide formed, for the production of sulfuric acid.

There are many roasting systems dependent on the particular equipment employed and the zinc extraction process which follows. These range from sintering to hearth and fluidised bed roasting systems. Sintering is generally used in preparing materials for pyrometallurgical production processes such as the blast furnace where hard lump material is required. It is not so suited to subsequent leaching operations where extensive grinding would be required. For such operations it is preferable to retain the material in a finely divided form.

To some degree the development of processes for the direct leaching of sulfides in acid solutions using oxygen, either directly as with pressure leaching, or indirectly as with ferric or cupric ion leaching, has overcome the need for roasting. However, as the application of these processes has demonstrated, roasting does have advantages in the elimination of certain impurities detrimental to the electrolytic process, particularly halides. Such impurities are volatile and are separated with roaster gases. The production of sulfuric acid may be both an advantage in contributing a valuable by-product, or may be a disadvantage where markets and outlets for sulfuric acid are difficult to find. This latter factor will be the major determinant for selection between roast-leach or direct leach alternatives, but in general, where acid markets are readily available, the roast-leach alternative is preferred.

PROCESS CHEMISTRY AND THERMODYNAMICS

The principal reactions involved in the oxidation of zinc sulfide concentrates are:



In addition, reversible sulfation reactions can occur as follows:



Relevant thermodynamic data for the above reactions are given in Table 4.1.

TABLE 4.1
Thermodynamic data for principal reactions.

Reaction No	Heat of reaction at 25°C as kJ per g mole of Zn	Free energy of reaction at 25°C as kJ per g mole of Zn
4.1	-865	-699
4.2	-678	-652
4.3	-456	-434
4.4	-107	-15
4.5	-98	-70
4.6	-156	-171
4.7	-76	-11

The principal combustion reactions are strongly exothermic and can maintain high combustion temperatures. Reaction equilibrium is controlled by the partial pressures of oxygen and sulfur dioxide and may be expressed in terms of an equilibrium phase diagram as shown in Figure 4.1. This shows the stable phases present at respective oxygen and sulfur dioxide concentrations in roaster gas, and at two different temperatures of 1100°K (827°C) and 1300°K (1027°C) (Ingraham and Kellogg, 1963).

Figure 4.1 shows that under normal operating conditions, basic zinc sulfate will be formed at 827°C but only zinc oxide at 1027°C.

In addition to zinc sulfide the mineral concentrate contains a range of other metal sulfides as impurities, such as FeS, FeS₂, PbS, CuFeS₂, CdS, MnS, etc.

Normal roasting conditions generally lead to the following primary reactions:

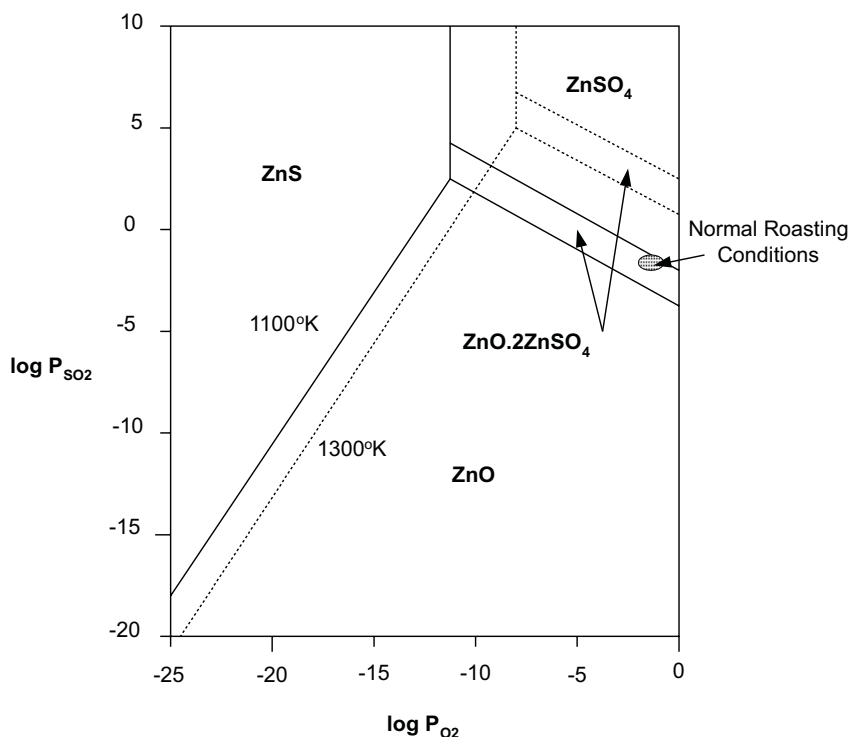
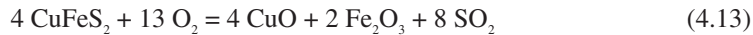


FIG 4.1 - Equilibrium phase diagram for Zn - O - S (pressure in atmospheres).



The degree of sulfate formation, as for zinc, depends on the concentration of oxygen and sulfur dioxide in roaster gas and the equilibrium balance for the reversible SO_3 formation Equation 4.5 above, which is dependent on the gas temperature. The equilibrium constant for Equation 4.5 is given by Equation 4.14.

$$\text{Equilibrium constant} = K_p = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} * \sqrt{(P_{\text{O}_2})}} \quad (4.14)$$

where p is the partial pressure of each component in atmospheres.

The correlation of the equilibrium constant with temperature is given by the expression:

$$\text{Log}_{10}(K_p) = \frac{4956}{T} - 4.678 \quad (4.15)$$

where T is the temperature in °K (Duecker and West, 1959).

For a roaster gas of ten per cent SO_2 and four per cent O_2 , and for a gas diluted with secondary air such that the composition becomes eight per cent SO_2 and 7.4 per cent O_2 , the equilibrium conversion of SO_2 to SO_3 may be given as in Figure 4.2.

This data suggests that at roasting temperatures of 950°C a conversion of six per cent SO_2 to SO_3 is possible, but in fact the actual is significantly below this due to the slow rate of reaction. Figure 4.2 also illustrates the potential to increase SO_3 formation and cause sulfation of calcine entrained in the gas stream, as temperature is reduced in the boiler system. Sulfation of calcine is undesirable for sulfate

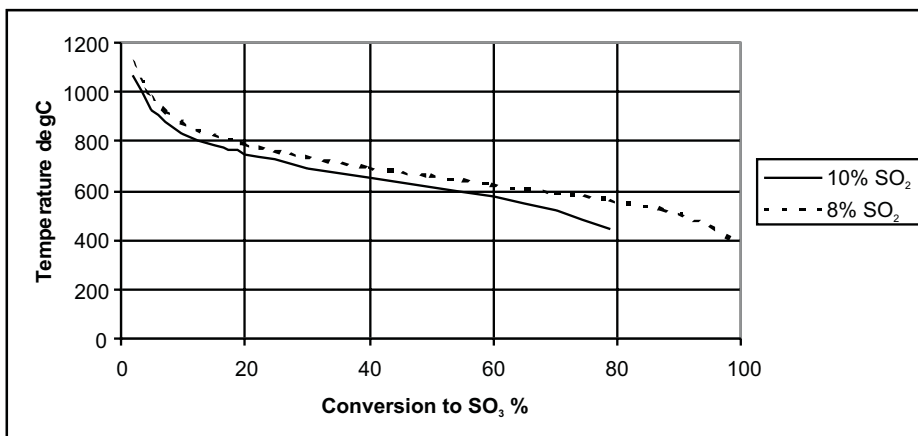


FIG 4.2 - Equilibrium conversion of SO_2 to SO_3 .

balance control reasons. The electrolytic plant solution circuit is closed and there is very limited outlet for sulfate ions, hence input of soluble sulfate such as zinc sulfate must be restricted. To achieve low sulfate levels in roaster calcine, it is important to keep oxygen levels low and the gas temperature high to minimise SO_3 formation. Generally, the rate of conversion is slow unless catalysed. Iron oxides in particular can act as catalysts and are present to a minor degree in calcines carried forward with roaster gases. It is therefore important to separate these solids as rapidly, and at as high a temperature as is possible. Rapid cooling of the gas will then reduce the rate of conversion of SO_2 to SO_3 to negligible levels below 350°C .

Minimum oxygen levels are preferred in limiting SO_3 formation but will lead to unconsumed sulfides in the calcine. Since it is desirable to reduce residual sulfides as sulfide sulfur to less than 0.5 per cent, some excess oxygen is necessary and is usually of the order of four to five per cent in roaster exit gas. However minor levels of sulfation will still occur.

The stability of sulfates and hence the ability to form may also be indicated by the temperature at which significant decomposition can occur under usual roaster gas composition, and is indicated in Table 4.2. If roasting temperature is above the given decomposition temperature then little of that particular compound is likely to be present in the calcine.

Solid State Reactions

With the exception of the SO_2 to SO_3 reaction (Equation 4.5), all the above reactions are heterogeneous gas-solid reactions. In addition to

these, a number of important solid state reactions occur during roasting. In particular these include the formation of mixed oxide 'spinel' type structures of the general form $\text{M}^{\text{II}}(\text{M}^{\text{III}}\text{O}_2)_2$ where M^{II} can be Mg, Zn, Cd, Mn, Fe, Co, Ni, and M^{III} can be Al, Ge, In, Fe, Co, Cr. In particular such compounds of iron or 'ferrites' are of importance in zinc roasting since they are quite stable under dilute acid leaching conditions, thus limiting the potential to extract zinc from roaster calcine under such conditions.



Any iron present in solid solution within sphalerite and referred to as 'marmatitic iron' will be fully converted to zinc ferrite (see Chapter 3). A significant proportion of free ferric oxide derived from pyrite and pyrrhotite will also react with zinc oxide to form ferrites and this reaction is favoured by increasing roasting temperature and residence time. In general, it is likely that over 90 per cent of iron contained in zinc concentrate will normally be converted to ferrites at temperatures over 900°C . Ferrites can be readily sulfated and hence with operation at lower roasting temperatures where sulfates can occur, the formation of ferrites can be minimised but at the expense of high sulfate levels in calcine, which is also undesirable from the viewpoint of sulfate balance control.

At lower oxygen partial pressures and higher temperatures, ferrites are also unstable and ferrite formation can be minimised. This situation occurs with the sintering process where ferrite formation is minimal and zinc solubility in dilute acid is high. However iron solubility in dilute acid leaching is also high which creates difficulties with the primary or neutral leach stage, and is the primary reason why sintering was not used as a roasting method for the electrolytic process.

The form of ferrite in terms of the degree of development of its crystal structure will affect its solubility in subsequent leaching operations. Fine, poorly developed ferrite is more easily leached and

TABLE 4.2

Decomposition temperatures of sulfates.

Compound	Decomposition temperature $^\circ\text{C}$
Fe_2SO_4	530
CuSO_4	620
ZnSO_4	670
$\text{CuO}.\text{CuSO}_4$	720
$\text{ZnO}.2\text{ZnSO}_4$	760
CdSO_4	840
PbSO_4	860
$\text{PbO}.\text{PbSO}_4$	>1000

is favoured by lower operating temperatures. In contrast, ferrites formed at high roasting temperatures are more difficult to leach under hot strong acid conditions.

The other important solid state reaction is the formation of zinc silicate.



This is favoured where there is a close mineral association of sphalerite and quartz within the mineral structure of the concentrates. Separate grains of quartz can also react with zinc oxide and depending on their crystal size, a significant proportion of the quartz can be converted. As for ferrite formation, the formation of silicates is favoured by higher temperatures and long residence times. Sintering in particular maximises silicate formation.

Acid soluble silicates such as zinc silicate give rise to difficulties in the leaching operation due to the precipitation of gelatinous hydrated silica, which interferes with settling and filtration operations. Hence, roasting conditions that minimise silicate formation are favoured. Generally this means placing limits on the content of silica in zinc concentrates.

The formation of lead silicates is also possible where galena and quartz are closely associated. This can cause difficulties due to its low melting temperature, particularly for fluid bed roasting operations. PbSiO_2 melts at 766°C whereas Zn_2SiO_4 melts at 1509°C .

Roasting Kinetics

The roasting of a concentrate particle may be described by a shrinking core model in which oxygen diffuses in through a gas boundary layer to the particle surface and then through an outer calcine layer to the sulfide mineral surface where it reacts. The reaction product SO_2 then must diffuse outwards against the incoming oxygen. The sulfide surface progressively retreats into the core of the particle and the diffusion path becomes greater.

Reaction rates for zinc sulfide may be catalysed by the presence of iron and copper sulfides and reaction rate constants will depend on the particular mineral composition, sizing and associations. Generally, chemical reaction kinetics control the oxidation rate for temperatures up to a transition temperature of around 600°C . Beyond this point the oxidation rate is controlled by diffusion through the boundary layer and through the calcine layer. The point of transition is governed by the particle size, and the transition temperature increases with decreasing surface area.

For relatively low roasting temperatures of around 800°C , boundary layer diffusion is the predominant control at low levels of conversion of sulfide to oxide, changing to internal diffusion control at high levels of conversion where the oxide layer thickness has increased. Whereas at higher roasting temperatures, boundary layer diffusion becomes less significant and the rate limiting step is essentially internal diffusion throughout the sulfide to oxide conversion range. High particle temperatures can promote the rate of oxidation due to the volatilisation of zinc sulfide, which occurs above 1020°C . There is evidence that zinc sulfide then tends to diffuse outwards and oxidise at the surface of the particle to form a separate outer oxide shell and gives rise to the formation of hollow spheres. However, results of oxidation tests on single particles show a marked reduction in the oxidation with a minimum around 1100°C due to the formation of a dense zinc oxide shell, effectively restricting diffusion and blocking the oxidation reaction. This is probably more relevant to sintering rather than concentrate roasting for subsequent leaching (Denbigh and Beveridge, 1962).

At more normal fluid bed roasting temperatures of 900 to 1000°C , the calcine particles tend to be a uniform ZnO matrix with any residual sulfur at the particle core. Some iron is retained in solid solution within the zinc oxide, but iron tends to migrate to the outside of the particle forming a distinct zinc ferrite phase. This separation of iron and formation of zinc ferrite at the particle boundary is more pronounced at longer retention times (Chen and Dutrizac, 2004).

Oxygen and Air Requirements for Concentrate Roasting

Based on the expected reactions outlined above, the oxygen requirements for a typical zinc concentrate of 51 per cent Zn, two per cent Pb, 0.5 per cent Cu, eight per cent Fe and 32 per cent S, may be calculated as shown in Table 4.3. This calculation is based on the roasting of 1000 kg of concentrate and the production of a calcine containing 0.5 per cent residual sulfide and 1.5 per cent S as sulfate. The concentrate has been subdivided into its mineral components for the purpose of the calculation as shown below. The distribution of iron between FeS and FeS₂ is determined by the sulfur balance, and gangue minerals are assumed to be inert towards oxygen.

ZnS	76.0 %
PbS	2.3 %
CuS	0.75 %
FeS	7.4 %
FeS ₂	7.05 %
Other – gangue	6.5 %

TABLE 4.3
Calculation of oxygen required for roasting and SO₂ formation.

Concentrate used	Calcine formed	SO ₂ formed	Oxygen Required
ZnS = 13.8 kg	ZnS = 13.8 kg		
ZnS = 714.2 kg	ZnO = 596.9 kg	469 kg	352 kg
ZnS = 32.0 kg	ZnSO ₄ = 53.0 kg		21 kg
PbS = 23.0 kg	PbSO ₄ = 29.3 kg		6.3 kg
FeS = 74.0 kg	Fe ₂ O ₃ = 67.3 kg	53.9 kg	47.2 kg
FeS ₂ = 70.5 kg	Fe ₂ O ₃ = 46.9 kg	75.3 kg	51.8 kg
CuS = 7.5 kg	CuO = 6.3 kg	5.0 kg	1.9 kg
Other = 65.0 kg	Other = 65.0 kg		
Total = 1000 kg	878.5 kg	603.2 kg	480.2 kg
Volume =		211 Nm ³	336 Nm ³

Note: For the purpose of calculating oxygen demand, zinc ferrite has been taken as its components – ZnO and Fe₂O₃ and not as a separate species.

To supply the required 336 Nm³ of oxygen per tonne of concentrate would require 1600 Nm³ of air. Some excess is required to ensure a high degree of oxidation of sulfide sulfur, and in practice the exit gas from the roasting operation contains of the order of five per cent oxygen. This would raise total air supply to the roasting stage of 2060 Nm³/t (including secondary air) and will give a roaster gas of 1935 Nm³ containing five per cent O₂ and 10.9 per cent SO₂. This represents the dry gas analysis and does not account for any water content, which arises from the water content of zinc concentrates as well as any water added to the roaster for temperature control purposes.

ROASTING METHODS

Hearth Roasters and Early Forms of Roasting Equipment

The first types of furnace for roasting sulfides were hand rabbled hearth furnaces of which the Delplace type was an example. This consisted of six to ten hearths one above the other with the bottom hearth fuel fired. Sulfide concentrates were fed to top hearth and hand raked from one end to a hole at the other end

where the material dropped to the hearth below. This approach was replaced by mechanical raking as in the Ropp Furnace, which used an endless chain carrying rakes to move material along the hearth.

An important advance came with the development of the circular multi-hearth design such as the Wedge, Skinner and Herreshoff designs. These furnaces use a central shaft equipped with two or four air cooled arms holding a series of rabble blades, which turn over and move the material radially and alternately inward to a central drop hole and outward to a peripheral drop hole (or holes). Normally for complete combustion of sulfides, fuel must be burnt in the lower hearth. Oxygen is supplied by excess air to the lower burners, by air passing through the rabble arms, and by air ingress through shell openings and doors. Bulk gas flow is countercurrent to the flow of solids. The top hearth usually serves as a drying hearth and ignition commences on the second hearth. This type of roaster may have from six to 16 hearths.

With efficient hearth roasters it is possible to produce a gas of around six per cent SO_2 but it is difficult to get below three per cent residual sulfides in the calcine unless fuel firing is used in the lower hearth when less than 0.5 per cent is possible. Operating temperatures used range from 800°C in the lower hearths to a maximum of around 920°C , which usually occurs on the third or fourth hearth.

Dust carryover is normally of the order of ten per cent to 20 per cent of feed.

The Hudson Bay Mining and Smelting Company operated a split draught hearth roaster at the Flin Flon plant in Manitoba. Gases from the top three hearths left the roaster at the top, while gases from the lower hearths were directed to a bottom flue. This maintained temperature on the bottom hearth without the need for fuel firing. Capacity was however lower than for other comparable furnaces.

Typical hearth roaster size was six metres in shell diameter with 12 hearths and performance on zinc concentrates as follows:

- 200 kg of sulfur oxidised per square metre of hearth area per day (or 0.7 t of concentrate per m^2 per day);
- gas strength of four per cent to six per cent SO_2 ; and
- residual sulfide sulfur in calcine typically around one per cent with fuel firing on the lower hearth.

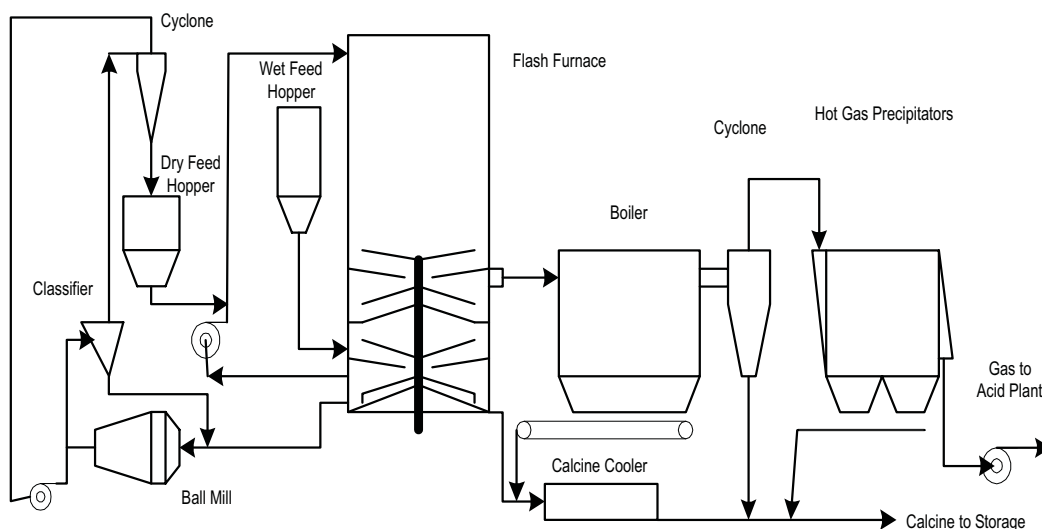
In some older electrolytic zinc flow sheets using Hearth Roasters, a flotation stage was incorporated in the leaching circuit to recover unburned sulfides from primary leach residue. The concentrate so produced was returned to the roaster.

Suspension or Flash Roasting

In this type of roaster, finely ground dry concentrates are conveyed with air and are blown into a hot combustion chamber which is maintained at around 950°C . The separate particles burn rapidly as they fall through the chamber and are collected on a rabbled hearth at the base of the chamber.

The process was developed by Cominco at the Trail smelter, British Columbia, and evolved by modification of a hearth roaster in which the upper hearths were removed. A typical flash roaster design had the tall open combustion chamber located above a series of hearths. One or two lower hearths were used for collection and desulfurisation, and one or two lower hearths were used for concentrate drying. Roaster gases exited at the base of the furnace. A typical configuration is shown in Figure 4.3 (Magoon, Metcalfe, Babcock and van Beek, 1990).

Concentrate was fed to the lower hearths, dried and then conveyed to an air swept ball mill where it was finely ground and air conveyed to the upper level burner. Dust loadings in gas from the furnace were high (at least 40 per cent of the feed). Combustion was quite efficient and under 0.1 per cent residual sulfides in calcine could be achieved. Roaster gas generally contained seven per cent to nine per cent SO_2 , but was particularly dusty in comparison with hearth roasters and required boilers specifically designed to handle the heavy dust loads. Generally Lamont type water tube boilers were used followed by cyclones.



The typical furnace size was six metre shell diameter with combustion chambers five to eight metres high. Capacity was typically five tonne of concentrate per square metre of grate area or cross sectional area per day, or up to 7.5 for larger units. Concentrates were ground to 95 per cent minus 325 mesh, requiring a significant power input.

Although the flash roaster had significantly greater capacity than the hearth roaster, it retained many of the mechanical features, which incurred high maintenance costs. The labour requirements to attend to much of the ancillary equipment were also high and from a cost viewpoint this equipment was rapidly replaced by the development of fluid bed roasting.

Fluidised Bed Roasting

Fluidisation concepts were first introduced to the chemical industry in the 1930s. This was extended to the roasting of pyrite and eventually to zinc concentrate roasting in the 1950s. There were a number of approaches to the design of the early fluid bed roasters, particularly relating to the method of feed addition, with the Dorr Oliver slurry feed system initially being popular. Improved designs for dry feeding by Vieille Montagne in Belgium and by Lurgi became the most favoured form of fluid bed roaster for zinc concentrate. The 'Lurgi' roaster has subsequently been used in most installation since the late 1960s.

Most recent advances have been with the ‘circulating fluid bed’ roaster, which has been applied to coal combustion and to pyrite roasting, but these principles had not been applied to zinc concentrate roasting by the end of the 20th century.

PRINCIPLES OF FLUID BED ROASTING

The fluidised bed roaster generally consists of a cylindrical chamber fitted with a lower grate to support a bed of fine particles and to distribute air uniformly across the roaster cross section. As the flow of gas through the fixed bed of particles is increased, the pressure drop across the bed and drag forces on the particles will also increase until these drag forces balance or exceed the weight of the particles when they will begin to lift. The bed then expands and the particles separate and become mobile. Separation reduces the particle drag coefficient, and a balanced position is reached at a particular bed expansion. At this stage, the particle bed resembles a fluid in its behaviour. The initial point of free particle motion is

the point of ‘incipient fluidisation’, and roughly equates to the point where the pressure drop across the bed equates to the weight of the bed per unit of cross section. If the flow is reduced at this point, the bed will settle back to a fixed packed bed, but at a more open packing density than the initial structure. This is illustrated in Figure 4.4 showing a plot of pressure drop as a function of gas flow.

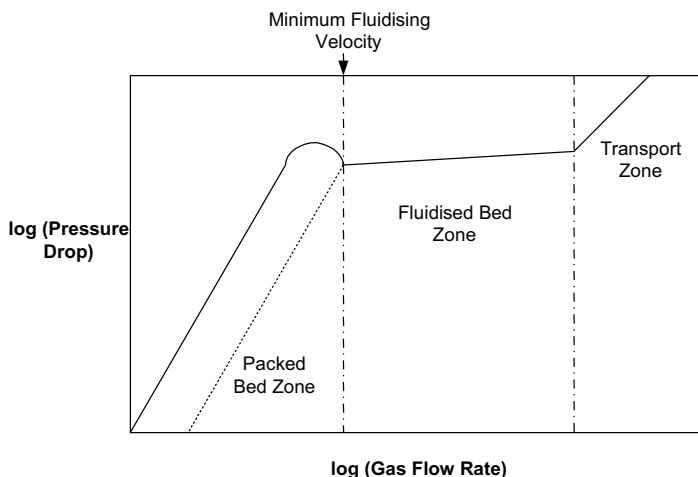


FIG 4.4 - Gas flow versus pressure drop for a fluidised bed.

An increase in gas flow beyond initial fluidisation will cause the bed to expand with little change in overall pressure drop. For gas-solid systems, the additional gas passes through as voids or bubbles, which form at the distributor plate, detach and rise up through the bed to burst from the upper surface flinging solids particles into the gas space above the bed. This behaviour does not generally occur with liquid-solid fluidised systems and whether two phase or bubbling flow occurs, depends on the relative density of the solids and the fluidising medium. If the difference is large bubbling will occur, which is the case for zinc roaster operation.

If the gas flow is increased, the bed will expand further to the point where individual particles are separated and are transported with the gas stream. A fluidised bed can then no longer be maintained. The turbulent layer roaster operates in the fixed bubbling bed regime, whereas the circulating fluid bed roaster operates in the transport region.

The normal turbulent layer fluidised bed is a complex heterogeneous flow system with gas flowing through the bed, both through the dense phase solids bed, and as bubbles. The heat and mass transfer rates are high within the dense phase due to the high degree of turbulence, and is a major advantage of the system.

In relation to the support or distributor grate, the relative pressure drop in comparison with the bed itself is of considerable importance in ensuring good gas distribution. The grate commonly consists of a ceramic lined plate with holes or nozzles of around 6 mm diameter and spaced at around 100 mm centres. This represents a gas flow area of about 0.3 per cent of the total grate area. The pressure drop across the grate should be at least 30 per cent of the total to ensure good gas distribution, otherwise there will be a tendency for gas to channel through one section of the bed leaving other sections static.

Particle size distribution effects

Of major importance to the performance of the fluidised bed system is the particle size distribution and the tendency for that size distribution to change as a result of chemical and physical reactions within the bed.

For a given gas velocity there will be a particle size defining minimum fluidising conditions, and a smaller particle size defining the point of independent support by the gas and the onset of transport. In simple terms these two particle sizes may be related to gas velocity by Equations 4.18 and 4.19 respectively (Themelis and Freeman, 1984).

$$V = \frac{D_1^2 * (\rho_P - \rho_G) * g}{1650 * \mu} \qquad \text{(Ergun Equation)} \qquad (4.18)$$

$$V = \frac{D_2^2 * (\rho_P \rho_G) * g}{18 * \mu} \qquad \text{(Stokes Law)} \qquad (4.19)$$

where
 D_1 = maximum sized particle to sustain fluidisation,
 D_2 = minimum sized particle which will not be transported,
 ρ_P = particle density,
 ρ_G = gas density,
 μ = gas viscosity, and
 g = acceleration due to gravity.

The above relationships are illustrated in Figure 4.5 for a typical air-zinc concentrate system.

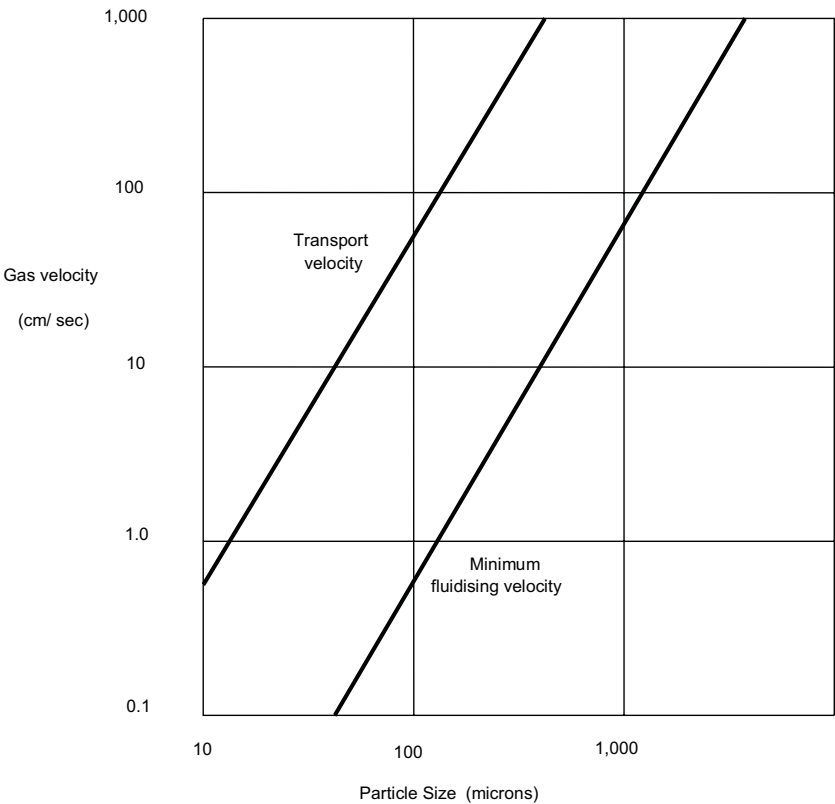


FIG 4.5 - Fluidisation diagram - extreme gas velocities.

Particles to the right hand side of the diagram with size greater than the minimum fluidisation line will settle out of the bed. Particles to the left hand side of the diagram and with sizes smaller than the transport velocity line will tend to be removed from the bed by elutriation. Particles sized between the two lines will form a stable fluidised bed. This representation is highly simplistic and other factors such as particle shape can have significant influence over the boundaries between zones which are by no means as clearly defined as indicated in Figure 4.5 (Szekely and Themelis, 1971).

For constant gas velocity, Equations 4.18 and 4.19 give the following relationship between the extreme particle sizes:

$$\frac{D_1}{D_2} = \sqrt{\frac{1650}{18}} = 9.6 \quad (4.20)$$

This indicates that the particle size ratio of coarsest to finest particles within a fluidised bed should be close to 10:1. Any particles coarser than this will tend to settle out on the grate of the roaster and any finer particles will tend to be elutriated from the bed. This is in fact a useful general rule for defining the optimum particle size range of bed material to achieve good fluidisation.

Particles below the minimum size and located within the transport zone of Figure 4.5 will initially be trapped within the structure of the dense phase of the bed, but if they are projected into the gas space above the bed by bursting bubbles they will be free to be carried away with the roaster gas. The probability that fine particles will be elutriated in this way will depend on their concentration in the bed. That is, the rate of elutriation is dependent on the concentration of particles of the particular size and it follows that for a batch system, the concentration will follow an exponential decay with time, as given in Equation 4.21.

$$\frac{\text{fines concentration at time}}{\text{initial fines concentration}} = e^{-kt} \quad (4.21)$$

where k = the elutriation constant.

For a continuous flow system, the proportion of material in the bed finer than the elutriation sizing will be significantly lower than the proportion in the feed. The residence time will also be significantly lower and to some extent dependent on the particle size.

At the other extreme, particles larger than the maximum size will tend to settle onto the roaster grate, and if in sufficient quantity, can cause a blockage and local defluidisation. If the chemical composition of the material is such that there is any tendency to form compounds with melting points below the operating temperature of the roaster bed and thus give rise to sticky particles, then such an accumulation on the grate and de-fluidisation can cause sintering. This is also a mechanism by which the particle size of the bed material can increase during operation. Unless there are means of removal of the coarser material it can tend to accumulate and progressively cause de-fluidisation. For this reason, solids may be removed by periodic tapping from the grate level as well as from the usual bed overflow.

Coarse particles will be lifted from the grate area by the effect of bubbles and can find their way to the overflow exit. This can be sufficient to maintain a fluid bed in the longer term provided the rate of input or *in situ* generation of coarse particles is low. Otherwise removal of solids at the grate level (using an underflow system) will be necessary to maintain the correct size distribution.

The other impact of particle sizing, apart from the extremes, is the actual distribution within the operating range. The distribution can affect the packing density and the mobility of individual particles within the dense phase of the bed. This can be expressed as the 'apparent viscosity' of the bed (which can be quantified using a paddle viscometer or flow characteristics). A uniform size distribution over the fluidisation particle size range of 10: 1 will give a highly fluid bed of low apparent viscosity. As the

distribution becomes less uniform and the proportion of fines increases, the viscosity also increases, which gives rise to a sluggish bed, favouring the formation of larger bubbles. The gas flow through the dense phase tends to be lower allowing more gas to by-pass through the bubble phase. This can in turn affect the combustion efficiency and lead to higher residual sulfides.

Optimum Particle Size Range for Zinc Concentrate Roasting

The preferred operating mode for a roaster is to be able to achieve complete combustion of sulfides and produce gas of maximum SO₂ content which is close to ten per cent. To do this the air required for combustion should be sufficient to support fluidisation. Combustion air required is of the order of 1600 Nm³/t of concentrate, for a concentrate of 51 per cent Zn, 32 per cent S and eight per cent Fe. Allowing for some excess oxygen, an air requirement might be of the order of 1700 Nm³/t.

If the concentrate feed rate is *T* t/h then the air rate required is 1700**T* Nm³/h.

Given:

Roaster grate area	=	<i>A</i>	(m ²)
Fluidising air velocity	=	<i>V_f</i>	(Nm ³ /m ² /sec)
Settled bed height	=	1.0	(m)
Bed material bulk density	=	1.2	(t/m ³)

Then:

Air required for fluidisation	=	<i>V_f</i> * <i>A</i>	(Nm ³ /sec)
	=	3600* <i>V_f</i> * <i>A</i>	(Nm ³ /h)

Operating the fluid bed only on the air required for combustion, and equating the air required for combustion with the air required for fluidisation gives Equation 4.22:

$$3600 * V_f * A = 1700 * T \tag{4.22}$$

or
$$\frac{T}{A} = \frac{3600 * V_f * 24}{1700} \tag{4.23}$$

$$= 50.8 * V_f \tag{t/m^2 per day}$$

The average residence time of solids in the bed can also be calculated as $\frac{1.2}{T/A}$ (hours), based on a one metre settled bed depth.

Based on Figure 4.5, and the gas velocity for a given size range, the roaster sizing or capacity in terms of the *T/A* ratio can be calculated together with the nominal residence time as shown in Table 4.4.

TABLE 4.4
Fluid bed design criteria as a function of particle size.

Particle Size Range (microns)	Gas Velocity (Nm ³ /m ² /sec)	T/A (t/m ² day)	Residence time per m of static bed depth (hours)
15 to 150	0.007	0.3	71.4
30 to 300	0.014	0.7	36.5
100 to 1000	0.15	7.6	3.3
150 to 1500	0.31	15.7	1.6
300 to 3000	0.82	41.7	0.6
600 to 6000	1.50	76.2	0.3

The practical range for a single stage operation is dictated by a T/A ratio at least comparable with other forms of roasting equipment to give cost effectiveness, and by a reasonable residence time to ensure efficient combustion of sulfur which can be short for fine particles but longer for coarse particles. Reasonable T/A ratios based on competitive flash or hearth roasters should preferably be above 5.0. Hence Table 4.4 indicates that for reasonable T/A ratios the sizing should be at least above the 100 to 1000 micron size range. Residence time requirements move in the reverse direction to the data given in Table 4.4, which shows shorter times as the size increases. Only sizes below the 150 to 1500 micron range would give reasonably practical residence times for efficient combustion. Taking both factors into account indicates that only the size range of 100 to 1000 microns satisfies all practical requirements. Although this calculation is a generalisation, it does indicate the basic design parameters for a single stage stationary fluid bed zinc concentrate roaster. Variations are possible by raising air supply and accepting lower strength SO_2 in roaster gas, or by oxygen enrichment of the fluidising air, thus lowering gas velocities for the same oxygen supply.

As an indicator of the suitability of bed material for control purposes, an index is often used such as the mass ratio of particles within the optimum 100 to 1000 micron size range to those greater than 1000 microns. The aim is to maintain that ratio as high as possible, and by experience for particular concentrates the tolerable minimum level of that ratio can be determined.

Control of Bed Particle Size Distribution

This is a particularly important aspect of the operation of fluid bed roasters. Primary control is exercised by sizing of the concentrate feed. Concentrates are produced by the fine grinding of ores to liberate the mineral constituents and generally average particle sizing would be less than 25 microns. Concentrates as received at the smelter are however much coarser due to agglomeration in the period following filtration. Agglomeration may be the result of relatively loose binding by water in the form of capillary forces, as well as by surface oxidation and the formation of zinc sulfate which can act as a strong binding agent. On injection into the hot roaster bed, the rapid vaporisation of water can cause decrepitation and breakdown of the agglomerate into smaller components. Concentrates which are highly reactive, often as a result of the presence of reactive minerals such as pyrrhotite, can be strongly agglomerated by oxidation during transport and storage, and can present to the roaster at quite a coarse sizing. This may require screening and size reduction of the concentrate before feeding to the fluid bed roaster. Screen sizing is usually around ten to 12 mm and it is particularly important that the screen size is not too large so as to avoid the introduction of too much coarse material, which will sit on the roaster grate causing de-fluidisation and bed instability.

Excessive fines below the elutriation size will be removed from the bed progressively and will report to boiler and cyclone dusts. A high proportion of fines and carryover can make it difficult to maintain a fluidised bed and due to the lower residence time of fine particles, can lead to elevated levels of residual sulfides in total product calcine. Carryover can be 60 per cent of the total production or above without affecting roaster performance. It is possible to retain more material in the bed by agglomeration of the feed simply by the addition of water to the concentrates followed by mixing to ensure that the water is uniformly distributed. The addition of zinc sulfate (eg as electrolyte) to form a binder can assist. The other means of achieving optimum and consistent size distribution is by feed blending. This also provides the ability to roast concentrates which could not otherwise be handled by the fluid bed roaster as separate materials.

Solids Mixing

The action of the fluid bed promotes thorough and rapid mixing of solids. Solids circulation in the vertical plane will be quite high due to the action of bubbles. This will tend to generate circulation cells across the bed section with solids carried upwards with bubbles in the centre of the cell and downward

at the edges of the cell. Transfer of solids across the bed will occur by turbulent motion within the dense phase at the edge of each cell with transfer from one cell to the next. Also solids will be thrown into the gas space above the bed by the action of bubbles and will fall back into adjacent cells as well as into the same cell. This will effectively result in the transfer of solids in the horizontal plane, but in general the rate of mixing in the horizontal plane will be significantly lower than in the vertical plane.

COMMERCIAL FLUID BED ROASTING EQUIPMENT

The configuration of the fluid bed zinc concentrate roaster as developed by Vieille Montagne and supplied by Lurgi, is shown in Figure 4.6. This is now the most common form of roaster used in electrolytic zinc plants and warrants particular attention. The roaster chamber is constructed with a larger diameter upper section to reduce gas velocity and serve as a de-entrainment zone and reduce the level of solids carry-over to the boiler system. Units range in grate area from 53 m² for the original designs to 123 m². Capacity is generally within the range of seven to nine tonne of concentrate per square metre per day or up to 1000 tonne per day.

A list of some commercial Lurgi-VM style turbulent layer zinc concentrate roaster installations is given in Table 4.5.

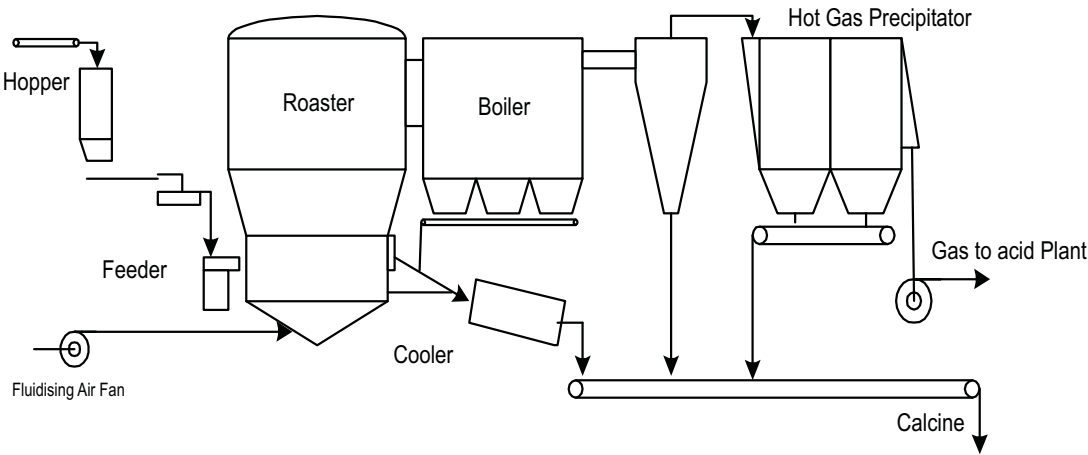


FIG 4.6 - Standard fluidised bed roaster assembly.

TABLE 4.5
Commercial Lurgi – VM type fluid bed roaster installations.

Plant location (See Table 1.3)	Number of units	Grate area m ²	Concentrate feed t/day	Feed as t/m ² /day
Auby	1	76	600	7.9
Aviles	1	42	300	7.1
	1	61	400	6.6
	1	123	850	6.9
Balen	1	50	359	7.2
	1	123	860	7.0
Budel	2	69	550	8.0
Cajamarquilla	1	100	720	7.2
Clarksville	1	65	500	7.7

Crotone	2	44	250	5.7
	1	55	350	6.4
Cartegena	1	35	220	6.3
Datteln	2	55	400	7.3
Eitreheim- Odda	1	37	250	6.8
	1	55	350	6.4
Hobart	1	55	420	7.6
	1	123	900	7.3
Juiz de Fora	1	46.4	410	8.8
Kidd Creek	2	56	356	6.4
Kokkola	2	72	500	6.9
Nordenham	1	90	650	7.2
Porto Vesme	1	77	480	6.2
San Luis Potosi	1	85	600	7.1
Townsville	2	77	610	7.9
Valleyfield	1	76	500	6.6

Concentrate Feed Blending and Feeding Methods

It is recognised that feed blend stability is an important issue for maintaining roaster stability and much attention is given to ensuring that the concentrate feed is a consistent mix of available raw materials. Blending is also used to ensure that composition and particle sizing are maintained within acceptable limits. Blending methods may simply use mixing by bucket or grab loads of individual concentrates from separate stockpiles into a blending stockpile or hopper, from where it is conveyed to the roaster feed bins. Otherwise more elaborate layered stockpile blending systems or individual hopper blending and proportioning systems may be used.

In relation to feeding concentrates into the roaster, the most common approach used in Lurgi designs is to 'dry' feed concentrates by injection into the roasting chamber using a high speed belt operating at around 1000 m/min and aimed at projecting feed into the centre of the roasting chamber (slinger belt feeder). Feed is projected through an open port in the side wall above the bed level. There are generally two operating feeders on the larger units and one on the smaller units.

Feeding concentrates as a slurry is also used and was a feature of early fluid bed roaster designs by Dorr Oliver. In this case, a slurry of ground concentrate at around 78 per cent solids was pumped into the roaster above the bed level. Distribution of the feed was not as good as with the slinger belt feeder and the roaster suffered reduced steam production in the waste heat boilers. It is however, possible to seal the roaster chamber and prevent excessive secondary air input.

Concentrates have been injected through a screw conveyor or dropped into a sealed side chamber from a weigh feeder. These systems also have the advantage of allowing the roaster to be fully sealed with much closer control of gas conditions. However, they are less robust than the slinger belt system from an equipment maintenance and operational viewpoint.

Air Flows

Fluidising air is supplied from a centrifugal fan or blower into a plenum chamber or 'wind box' beneath the roaster grate. Wind box pressure is generally around 2.0 m water gauge to support a bed depth of around 1.5 m.

Because of the open feed ports, pressure in the roaster chamber is maintained under slight vacuum by means of the suction from the 'clean gas' fan located after the electrostatic precipitators. This means that a significant leakage of air occurs through the feed ports and through any openings in the boiler

system. The quantity of air leaking in through the feed ports is roughly 120 m³/t of concentrate feed. Air leakage into the boilers varies greatly depending on the cleaning practices and the integrity of the equipment. It can be of the order of 20 per cent of total gas flow.

These secondary air additions raise the oxygen level and can increase the chance of formation of SO₃, particularly in the boiler as the gas temperature is reduced. This in turn will give rise to some sulfation of carryover calcine.

Operating Conditions

Operating bed temperature is usually within the range of 900 to 980°C. If a large proportion of the feed is elutriated from the bed there can be excessive combustion above the bed and gas temperatures in the upper part of the roaster can exceed the bed temperature. The quantity of bed calcine that carries over is normally within the range of 40 to 60 per cent of the total. The distribution of calcine to various collection points will depend on the fineness and nature of the concentrate feed but may be typically as follows:

Bed overflow/ underflow	40 %
Boiler collection	30 %
Cyclone collection	20 %
Hot precipitator collection	10 %

The composition of these calcines will vary in terms of the content of volatile elements which tend to increase as the collection temperature reduces. There is a tendency for enrichment in cadmium, lead and silver as well as halides and sulfate moving through the collection chain.

The residence time of bed overflow solids in the roaster averages around four hours and for carryover solids around one hour. In the latter case most of that time is within the bed before being elutriated. Once elutriated from the bed, the residence time of solids in the gas stream is only a matter of seconds before drop-out and collection.

Temperature Control

Operating temperature is the primary control and dictates the stability and performance of the roaster. Control is by either the heat generation rate which directly relates to the concentrate feed rate, or by heat removal by means of fixed cooling coils inserted into the bed and by the heat content of the exit gas. The heat content of exit gas can be controlled to a small degree by the volume of fluidising air used, but to a major extent by its water content as controlled by the direct injection of water into the roaster or by the addition of water to the concentrate feed.

The cooling coils are integrated into the boiler system and generate steam. Cooling coils are inserted as a series of loop bundles through the roaster wall. Cooling surface area can be up to 40 per cent of the grate area, however a large cooling coil area does provide a large fixed heat removal rate and limits the ability to turn-down the feed rate of the roaster. Hence some balance of cooling coils and water injection is generally preferred to give greater flexibility in production rates. Water injection carries the penalty of generating additional gas volume to be handled by the boiler system and clean gas fan. It also reduces the amount of sensible heat which can be extracted by the boilers, thus reducing steam production, and it increases cooling loads on the downstream gas cleaning section prior to the acid plant.

As indicated earlier in this chapter, the addition of water directly to the concentrates can achieve some degree of agglomeration and assist in maintaining solids within the bed, reducing carryover. This effect is not influenced by direct injection of water into the bed or above the bed, which merely reduces total bed and gas temperatures. Water addition to the concentrate will reduce temperatures but will also reduce carryover and overbed combustion, and hence temperature elevation of exit gas above the bed temperature.

It is also possible to inject zinc sulfate solution as a bleed from the electrolytic plant solution circuit. This increases heat absorption by decomposing the zinc sulfate and hence reduces the quantity of water needed for thermal balance control. It provides a useful bleed of volatile impurities such as halides from the electrolytic circuit, but can increase the level of SO_3 in roaster gas with increased risk of forming hard accretions on the walls of the roaster chamber ('wall cake') and in the boiler. Wall cake formation is also aided by operation at elevated temperatures when 'sticky phases' can form. It can be particularly damaging if it dislodges during operation, falling onto and blocking the roaster grate. Generally wall cake builds up progressively during operation and is cleaned off during annual or biannual shutdowns.

The amount of secondary air entering through the feed ports impacts on the temperature of overbed gas and can reduce it well below the bed temperature if carryover of solids and overbed combustion is low. However, with a high level of fines carryover and combustion above the bed, exit gas temperatures can rise significantly. As indicated above, this can be controlled by the addition of water to the concentrates and generally gas offtake temperatures are held below 50°C in excess of the bed temperature. High offtake temperatures will tend to increase boiler accretions.

Stability of the roaster is indicated by the temperatures recorded by a number of thermocouples located throughout the bed. These should be uniform or within a range of no more than 10°C . If there is defluidisation in any section of the bed the thermocouples at that position will show a substantial decrease, which may be of the order of 100°C or more. This provides an indication of the onset of problems and the need for action to restore stable operation. Generally, defluidisation results from a coarsening of the bed material. The accumulation of such coarse material on the roaster grate creates 'dead' zones and can lead to sintering of the static material. Operating at excessive temperatures, particularly in the presence of low melting point phases, can be a significant cause of instability leading to failure.

Low melting point phases are particularly related to the presence of lead, silica and copper. Lead silicates provide a series of stable low melting point phases. Copper gives rise to low melting point copper mattes. A common general rule has been to ensure that the sum of the copper, lead and silica contents of the concentrate feed are below five per cent. However some plants have developed correlations between the contents of these elements in their particular feed and the maximum permissible bed temperature. This correlation is likely to be specific to the particular concentrate feed blend and roaster configuration.

Calcine Removal

Bed calcine overflows a weir located on one side of the roaster chamber opposite the feed ports. This maintains the bed level and is adjustable within a limited range by inserting or removing plates to raise or lower the weir level. Provisions are also made for removal of calcine from the roaster grate area through a tube fitted with a poker to control flow. Generally, withdrawal is intermittent on a time cycle and needs to be of sufficient frequency to keep the system operational and avoid blockage. Withdrawal of a significant proportion of bed calcine via the underflow poker will ensure that oversize solids are removed, that optimum bed particle sizing is maintained and that the risk of grate blockage is minimised.

Bed overflow and underflow calcine passes directly to a cooling device, either as a rotary or fluid bed cooler, prior to transfer to storage. Calcine collected by drop-out in the boilers, from cyclones and from electrostatic precipitators is collected using chain conveyors which may be water jacketed for calcine cooling.

Sulfur Elimination

The basic objective of roasting is to eliminate sulfur by oxidising sulfides to oxides as completely as possible. The fluid bed roaster will reduce residual sulfide sulfur to 0.5 per cent or less. The bed calcine

can contain down to 0.1 per cent, but the carryover material will be significantly higher and is very dependent on particular circumstances.

In addition, calcine will contain sulfur as sulfate. Usually all lead appears as sulfate otherwise the presence of any zinc sulfate or basic zinc sulfate (the most stable phase) will mainly be due to sulfation of zinc oxide by reaction with sulfur trioxide. This is quite low in bed calcines representing less than one per cent sulfur content, but increases in the carryover calcine as the collection temperature decreases. Thus the sulfur as sulfate in boiler calcine can be two to three per cent, cyclone calcines up to five per cent and hot precipitator material up to ten per cent.

Ancillary Equipment

The boilers are usually Lamont type with forced circulation water tube bundles, although membrane wall sections, particularly at the front drop out chamber, are now common. Because of the heavy dust loadings, mechanical cleaning of the boiler tubes and surfaces is necessary and a number of proprietary rapping devices as well as soot blowers are in use. Manual cleaning is often practiced on a regular basis to remove dust collection that cannot be dislodged by mechanical cleaning devices. Improved boiler designs aim to minimise the need for manual cleaning but the tendency for dusts to stick to the tubes varies greatly with the nature of the feed concentrates (Westerlund and Peippo, 1989).

It is possible to install hot cyclones before the boiler to reduce the dust load, but high temperature brick lined cyclones operating at over 900°C are heavy maintenance items and sealing of the drop leg carrying recovered calcine is troublesome with a high potential for blockage. Nevertheless this approach does significantly reduce the suspended solids load on the boiler.

The Russian approach of using a water jacketed vertical shaft from the roaster to serve as a pre-cooling and drop out chamber is another alternative which effectively reduces dust loads on the boiler.

Gas at the boiler exit is generally cooled down to 350°C, passes to a set of cyclones and then to electrostatic precipitators. The final temperature must be well above the dew point of sulfuric acid to avoid any condensation on the boiler tubes or internal boiler structures.

The precipitators usually consist of two parallel trains each consisting of two electric fields in series. Cyclones may be omitted, but the precipitators will then need to be designed for an increased load of the order of three times, and will require three fields in series. Dust loadings in the gas stream following the hot gas precipitators should be reduced to 50 mg/m³ or less.

Steam generation is typically 1.1 kg per kg of concentrate feed at 40 bar pressure superheated to 400°C, but steam production will depend on the analysis of the concentrate feed and the amount of water added to the roaster with concentrates or separately injected for temperature control.

The other important item of ancillary equipment is the calcine cooler. As indicated above, this may be a rotary cooler, water jacketed conveyor coolers or a fluid bed cooler. The rotary drum cooler is the most common approach. It consists of a rotating drum fitted with water cooled internal fins and directly receives bed calcines from the overflow weir, underflow pokers and from the boiler collection conveyor. It is generally linked with an independent water cooling tower.

Fluid bed coolers are also commonly used and consist of a gently fluidised bed of rectangular cross section fitted with cooling coils for generation of low pressure steam or for preheating boiler feed water. Fluidising air passes to the roaster as secondary air. This system will provide for increased heat recovery as steam and will marginally lower residual sulfides.

Oxygen Enrichment of Fluidising Air

By raising the level of oxygen in fluidising air, the capacity of the roaster can be increased for the same total gas flow. Heat generation within the fluid bed will increase without any increase in heat removal by exit gases, hence additional cooling coils will be required. There are limits to the cooling coil area,

which can be installed in a conventional fluid bed roaster, and hence there are limits to the degree of oxygen enrichment possible. With the standard turbulent layer roaster designs it is unlikely that oxygen can exceed 28 per cent in fluidising air. With such high oxygen inputs, the SO_2 level in roaster gas can rise to 15 per cent. These high concentrations can increase the chances of sulfation, particularly in the boiler, and increase the formation of accretions both within the roaster as wall cake and in the boiler, requiring increased cleaning. Indications are that a two per cent oxygen enrichment can increase the capacity of an average roaster by 15 per cent and cooling requirements must be increased by 50 per cent when supplied by water injection. Cooling issues will generally limit the application of oxygen enrichment (Saha, Scott Becher and Glums, 1989).

Calcine quality in terms of residual sulfide levels can be significantly improved by oxygen enrichment. However, in all cases, the cost of oxygen supply must be justified by the marginal improvements in calcine quality (and consequent zinc recovery for the total plant), or by the marginal improvement in plant capacity.

OTHER FORMS OF FLUID BED ROASTING EQUIPMENT

The 'Overpelt' Roaster

This roaster was originally developed by Metallurgie Hoboken-Overpelt at the Overpelt plant in Belgium for the purpose of providing pelletised feed to a horizontal retort zinc plant as a replacement for sintering. It was subsequently found to be suitable for providing calcine feed to an electrolytic plant and has a number of advantages over the standard turbulent layer roaster (DeKeyser and Denoiseux, 1980).

The roaster is illustrated in Figure 4.7 and consists of a long rectangular unit 7.45 m long by 1.44 m wide and is 5.5 m high.

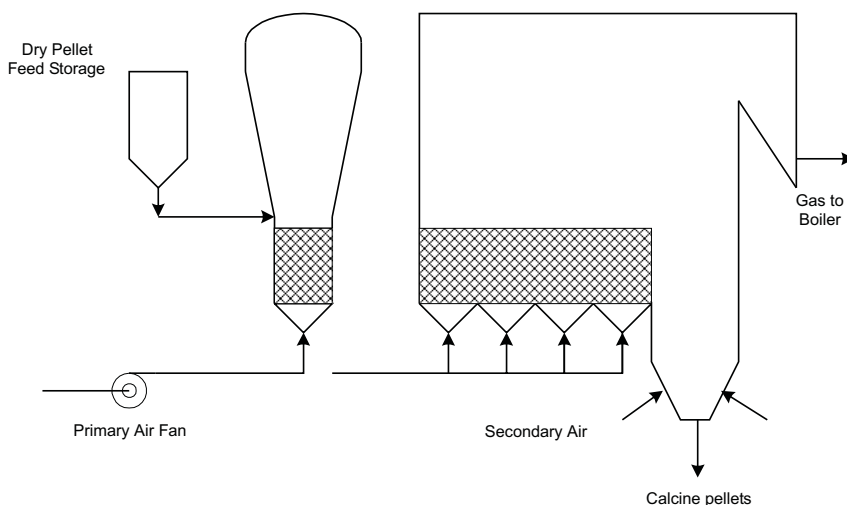


FIG 4.7 - The Overpelt roaster.

The primary feature of the Overpelt roaster is the roasting of pelletised feed and production of calcine in pelletised form. The advantage is its flexibility in terms of concentrate composition and sizing. Concentrate is pelletised by mixing with recycle oxides and sulfuric acid to form a zinc sulfate binder. Weak acid from the roaster gas cleaning plant is suitable for this purpose. The pellets are formed

using a disc or drum pelletiser and are dried in a fuel fired rotary drum dryer. Fuel consumption is the equivalent of 15 kg of fuel oil per tonne of pellets and the associated cost is a significant disadvantage of this process. Pellets are screened at between 0.5 and 4 mm to provide roaster feed.

The roaster grate is divided into six individual wind boxes each of 1.8 m² grate area. Pellets are fed at one end and overflow at the far end with a residence time of about one hour. Air rates in each wind box can be varied to control the temperature profile, which is normally between 1000 and 1060°C. The calcine overflows into an open chamber where it is semifluidised with cold air to drop the temperature to 400°C.

Roaster gas passes to a normal boiler system followed by electrostatic precipitators. Approximately 20 per cent of calcine is carried over to the boiler system.

In comparison with the standard turbulent layer roaster, this unit has a highly stable bed, which, due to high gas velocities, shows no tendency to sinter and therefore can process a wide range of concentrate compositions, for example with lead and copper contents over 20 per cent. Sulfur elimination is high with residual sulfide sulfur levels below 0.15 per cent and sulfation is also low due to the high operating temperatures and low carryover of calcine to the boiler. Halide elimination is also highly efficient.

Furnace capacity is high at 25 t per day per square metre of grate area, and start-up and shut-down flexibility is high, with start-up to operating temperature within two hours. Because of the permissible range of operating gas velocities, a high level of oxygen enrichment (to 30 per cent in fluidising air) is also possible to further increase capacity.

The disadvantage is the need to pelletise and dry the feed material and the need for extensive grinding of the product calcine prior to leaching. The Overpelt electrolytic zinc plant was closed in the mid 1990s and no roaster of this type continued to operate after that time. Nevertheless this form of roaster does illustrate the possibilities for processing difficult and complex concentrates, which may not be handled by a conventional turbulent layer roaster.

The Circulating Fluid Bed Roaster

The circulating fluid bed roaster operates at gas velocities within the dilute phase transport regime. The grate area is much smaller and gas velocities are much higher than for the static turbulent layer roaster.

The roaster configuration is shown in Figure 4.8.

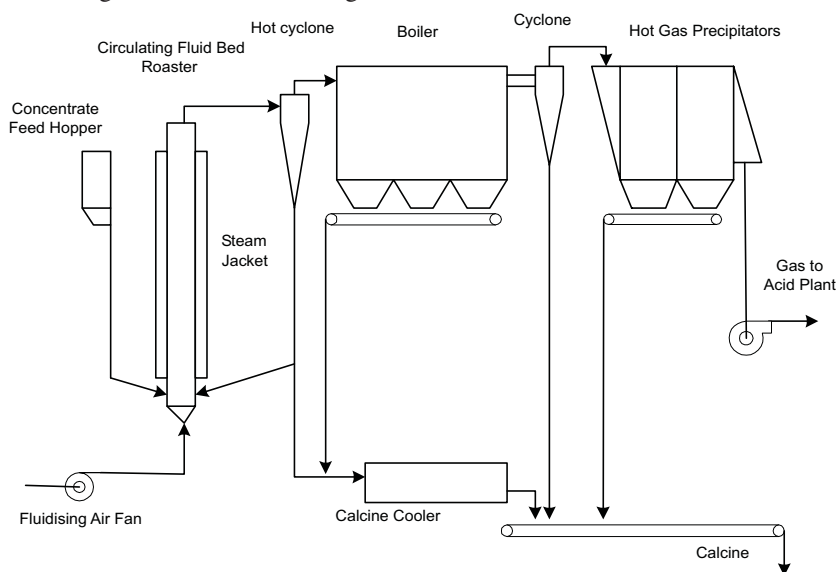


FIG 4.8 - Circulating fluid bed roaster.

The roaster vessel consists of a tall cylindrical chamber which can be jacketed as a membrane wall boiler. Roaster gas passes from the top of the chamber to cyclones and then to a conventional boiler system. The cyclones separate calcine which is returned back to the grate of the roaster, hence building a circulating load of solids. New concentrate is injected at the grate together with recirculated calcine from the cyclones. Part of the calcine stream from the cyclones is separated as product calcine.

The advantages over the standard turbulent layer roaster are the reduced size and hence capital cost of the roaster vessel, the improved flexibility in terms of the sizing and nature of concentrates which can be handled, and the simplified thermal control and heat recovery efficiency within the roaster itself. All feed handling, boiler, gas handling equipment and calcine cooling and handling equipment are similar to the conventional turbulent layer roaster. This system has been applied to the roasting of pyrite concentrates but there were no applications to zinc concentrate roasting by the early 2000s.

ROASTER GAS PROCESSING

Roaster gas contains carryover calcine dust and a range of volatile elements which must be removed before gas is of sufficient purity for use in the production of sulfuric acid by the catalytic conversion process. Gas is usually of the order of nine to ten per cent SO_2 and will normally contain calcine dust at around 50 mg/m^3 . Chlorine, fluorine, mercury and selenium are the principle volatile impurities associated with the roasting of zinc concentrates and which need to be removed.

Mercury contaminates product acid and maximum limits are usually specified at between 0.5 and 1.0 ppm. Without separation, and depending on the individual concentrate, the mercury level in product sulfuric acid can range upward from 10 ppm to 50 ppm or more. Mercury removal is therefore an essential part of any gas cleaning procedure.

Halide removal, particularly of fluorine, is important due to its attack on brickwork and the acid conversion catalyst, as it causes degradation of the catalyst carrier which in turn raises pressure drop and can limit gas flow.

A generalised flow sheet of gas cleaning is shown in Figure 4.9.

The first stage of gas purification is a combined scrubbing-cooling stage. Many devices are used such as spray towers, packed towers, plate scrubbers such as the Peabody Scrubber, or a venturi scrubber. Scrubbing liquor is circulated through the scrubbing system and becomes acidic due to the absorption of SO_3 contained in roaster gas. This results in a significant loss of sulfur recovery and an increased load on any subsequent effluent treatment facility, and hence places importance on minimisation of SO_3 formation in the roasting plant.

Often the scrubbing system consists of two stages, with the first as a quench or humidifying stage to reduce gas temperature from 300°C to less than 100°C , followed by a second scrubbing - cooling stage which lowers the temperature to less than 40°C . The final temperature is important

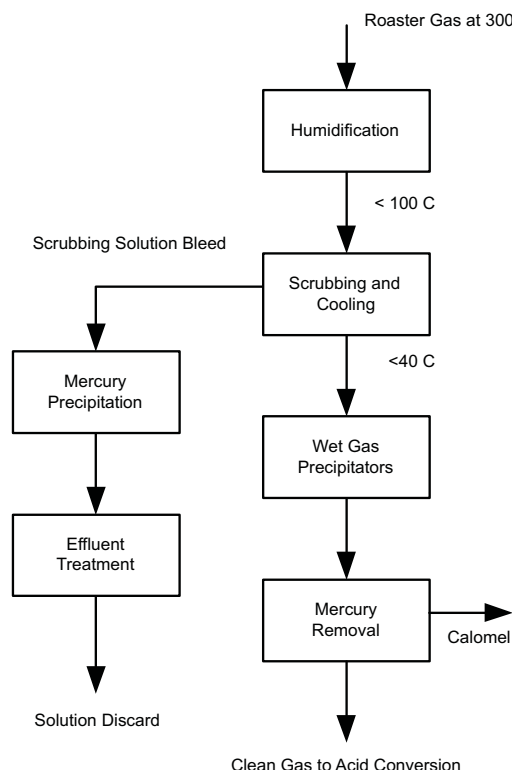


FIG 4.9 - Generalised flow sheet of roaster gas cleaning.

since the gas will be saturated with water vapour and the temperature determines the amount of water going forward to acid production, which must be less than that required to combine with the SO_3 formed. Hence there is a direct relationship between the SO_2 content of the gas and the maximum temperature of that gas leaving the scrubbing system, as shown in Table 4.6.

There are also benefits in lower scrubbed gas temperature since the vapour pressure of other volatile impurities (such as mercury) will also be lowered.

The 'weak acid' scrubbing liquor containing sulfuric acid as well as chlorides and fluorides is very corrosive and appropriate materials of construction must be used. One particular area of high corrosion potential is the boundary region where hot gas first meets scrubbing liquor. This is usually a troublesome and high maintenance area for the containment equipment.

The weak acid scrubbing liquor is bled from the system to maintain either a preset maximum acidity or a maximum fluorine concentration. Otherwise the bleed will merely be set by the water balance control. This solution also contains zinc and cadmium dissolved from calcine dusts as well as mercury and selenium. Mercury and selenium react to form mercuric selenide, which precipitates and can foul heat transfer surfaces. The presence of selenium can be beneficial in increasing the capture of mercury by the gas scrubbing system, however the amount of selenium is generally relatively low in comparison with the mercury content of zinc concentrates.

In some instances, the scrubbing system includes a final stage of sacrificial silica packing to ensure full capture of fluorine and to protect the acid conversion catalyst.

Following scrubbing and cooling, suspended droplets of scrubbing solution or mist are removed in wet electrostatic precipitators. The cleaned gas will still contain unacceptable levels of mercury vapour which must be removed before transfer of gas to the acid conversion plant. There are a number of mercury removal techniques but the most commonly used is the Boliden-Norzink Mercury Removal Process which uses mercuric chloride solution to scrub the gas and absorb mercury according to Equation 4.24 (Dyvik, 1985).



Mercurous chloride or calomel is insoluble and precipitates from solution. It can be separated in a thickener and removed from the system. Part of the calomel is treated with chlorine to regenerate the mercuric chloride scrubbing solution. The system is capable of achieving less than 0.5 ppm mercury in product acid or lower if reduced gas temperatures are used. It is important for efficient operation that the gas coming forward from the electrostatic precipitators is free from suspended mist and is classed as 'optically clear', otherwise contamination of the mercury scrubbing circuit will quickly destroy mercury removal efficiency.

Following mercury removal, the gas is suitable as feed to a conventional wet gas sulfuric acid plant of which there are many designs and configurations. This clean gas should be capable of production of high quality sulfuric acid.

The 'weak acid', or scrubbing solution bleed, represents a disposal issue and is usually sent to an effluent treatment facility where the acid is neutralised with lime to form gypsum and the metals are precipitated. Prior to neutralisation, SO_2 is stripped from the bleed solution with air and the mercury content is removed, usually by sulfide precipitation.

TABLE 4.6

Temperature of wet gas as a function of SO_2 content.

SO_2 content of roaster gas%	Maximum Temperature of wet gas to acid production °C
10	44.5
9	42.4
8	40.1
7	37.5
6	34.5

Following neutralisation and removal of base metals, the final solution containing chlorides can be discarded, provided it meets relevant environmental standards. The gypsum solids may be leached with dilute acid to recover zinc and cadmium for return to the electrolytic zinc plant circuit, although there are many different flow sheets depending on individual smelter situations and the opportunities for waste disposal. To avoid neutralisation and gypsum production, it is possible to return weak acid solution to the electrolytic zinc circuit, however it is important that the halides and other minor impurities are first separated and that outlets are available. The handling of the weak acid stream does present difficulties for many operations and it is important that quantities are minimised by attention to reducing SO_3 formation in the roasting plant and reducing dust carryover from the hot precipitators.

SULFURIC ACID PRODUCTION

Generally the sulfur dioxide concentration in gas from zinc roasters is in the optimum range for sulfuric acid production by the contact process, and this type of plant is universally used. Sulfur dioxide is oxidised to sulfur trioxide at temperatures of around 400 to 500°C over a vanadium pentoxide catalyst. Resulting SO_3 is absorbed in strong sulfuric acid and reacts with contained water to form H_2SO_4 .

The first stage of the acid plant involves drying the gas and added air in a packed tower (Drying Tower), where it is contacted with 93 to 96 per cent sulfuric acid at a temperature of around 65°C. Acid is circulated between the drying and absorption towers to maintain the acid strength in the drying tower and feed water into the absorption tower circuit. This provides most of the water required for the formation of sulfuric acid by reaction with SO_3 . Hence there are limits on the moisture content of input gas as detailed in Table 4.6.

Dry cold gas usually then passes through the gas blower, is heated to 420°C and passes to the first catalyst pass. The oxidation of SO_2 to SO_3 is exothermic and gas exiting the first pass may be of the order of 600°C. Heat is extracted by heat exchange with incoming cold gas before transfer to the second catalyst pass. There are many different arrangements of heat exchange between incoming cold gas and the various gas streams to and from the catalyst beds, dependent on the particular plant design. At least three, but more commonly four, catalyst beds are used, and it is generally aimed to operate at temperatures between 420 and 450°C.

Following the third catalyst pass, gas is treated in the interpass absorption tower to absorb SO_3 . Exit gas from the interpass tower is reheated by heat exchange and passes to the fourth catalyst bed for conversion of residual SO_2 and then to the final absorption tower. With this double absorption system, SO_2 conversion can exceed 99.5 per cent.

A flow sheet of a typical sulfuric acid installation is given in Figure 4.10.

Single absorption is also used but achieves lower conversion at 98.0 to 98.5 per cent, and emissions of SO_2 in tail gas are much higher (five times). Unless tail gas scrubbing is applied, single absorption plants will generally not meet normal environmental emission standards.

Controlled water additions are made to the final absorption circuit to control product and circulating acid strength at 98 to 98.5 per cent H_2SO_4 . Insufficient addition will result in oleum formation with high corrosion potential as well as the potential for fume generation.

Acid circulating over the absorption and drying towers must be cooled by heat exchange with cooling water and represents a significant thermal load of low grade heat. Plate exchangers are most commonly used for this duty but shell and tube exchangers are also common. It is important to closely control the temperature of circulating acid for optimum performance of the towers and to prevent the generation of fine mist or SO_3 fume which can carryover into tail gas. Absorption tower acid is generally controlled within the range of 80 to 90°C and high efficiency candle mist eliminators are used to minimise carryover.

Some more recent plant designs operate the interpass tower at high temperatures (180°C) so as to enable cooling by the generation of low pressure steam for improved by-product heat recovery.

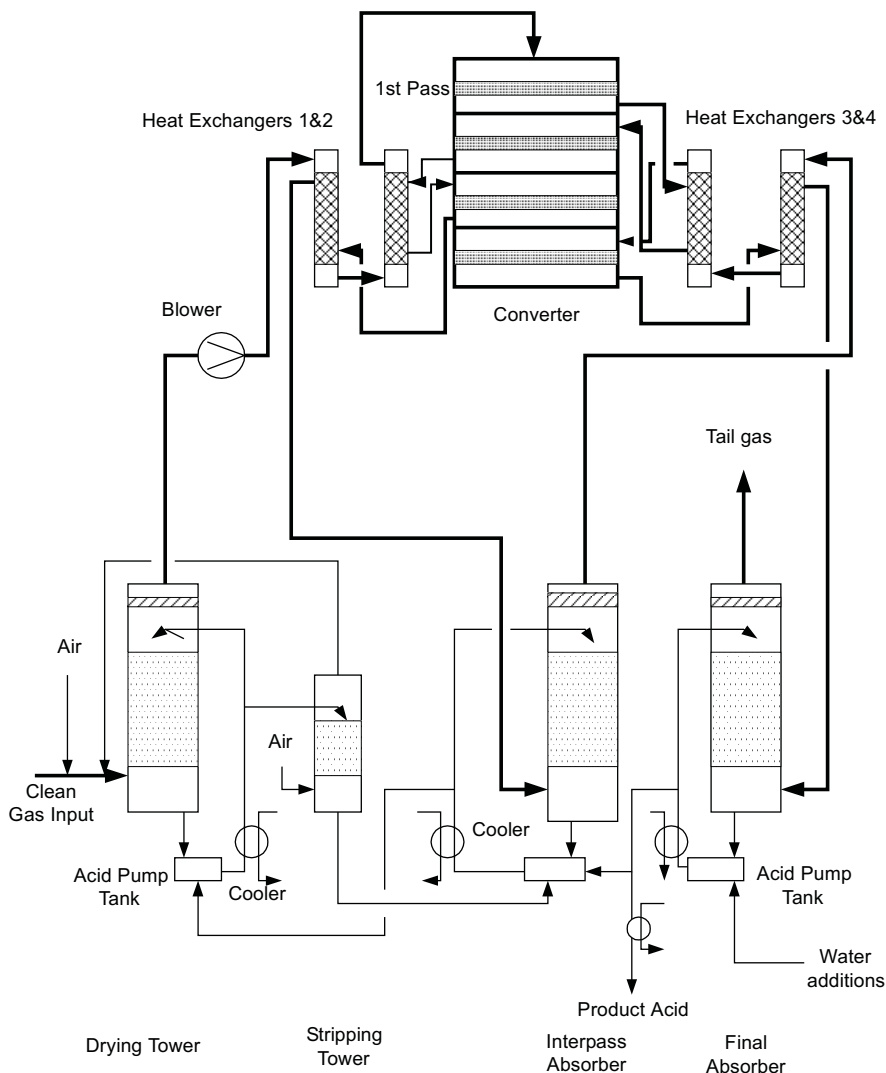


FIG 4.10 - Typical sulfuric acid plant flow sheet.

However conditions are highly corrosive and careful selection of materials of construction are required with close control of operating conditions.

Product acid is drawn from the final absorption tower circuit and is cooled to 40°C before storage in mild steel tanks.

Apart from the emission of SO_2 in tail gas there can be a problem with oxides of nitrogen (NO_x). This appears to be a function of the nature of the concentrates roasted and is particularly apparent from concentrates with a high carbon content. It can also occur if plant solutions containing ammonia are injected into the roaster, and can be common in plants operating the jarosite process. To some degree NO_x can be controlled by separating and treating acid drainage from the absorption tower candle mist filters, but if the problem is severe it may be necessary to install a separate catalyst bed to decompose nitric oxides in the main gas stream.

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Leaching and Solution Preparation

PURPOSE

The objective of the leaching operation is to dissolve zinc as selectively as possible to form a solution suitable for electrowinning following appropriate purification procedures. Electrolytic zinc processes almost exclusively use sulfate solutions and hence the leaching operation involves the dissolution of zinc from calcine using sulfuric acid in the form of spent electrolyte. It is also possible to leach zinc directly from sulfide concentrates without prior roasting and this is detailed later in this chapter. However the leaching process generally uses calcine as the primary feed and is simply based on the acid-base reaction as shown in Equation 5.1.



Sulfuric acid is supplied in the form of spent electrolyte after electrowinning and commonly containing around 150 g/L sulfuric acid and 50 g/L zinc, although these levels will vary from one plant to another.

Equation 5.1 describes the Primary Leaching operation. In addition, the presence of zinc ferrites requires more severe leaching conditions and a Secondary Leaching step is needed to extract residual zinc from the Primary Leach Residue.

LEACHING OF CALCINE

Although calcine contains zinc mostly in the form of zinc oxide, it also contains zinc in the form of zinc ferrite, zinc silicate and to a minor extent as residual sulfide (see Chapter 4). The attack on the various compounds during leaching and the dissolution of zinc is determined by the acidity of the leach solution and its temperature. Four broad leaching regimes are commonly employed:

- neutral leaching in the pH range of 4.0 to 5.5 and at around 60°C,
- weak acid leaching from 10 g/L H_2SO_4 to pH 4.0 and at around 60°C,
- hot acid leaching from 30 to 80 g/L H_2SO_4 and at over 90°C, and
- strong acid leaching at acidities above 120 g/L H_2SO_4 and at over 90°C.

These regimes are applied in a multi-stage countercurrent format. The first two stages of neutral leach and weak acid leach are often referred to as 'primary leaching' and leave a residue essentially containing zinc ferrites. The hot acid leach and strong acid leach are referred to as 'secondary leaching' and are integrated with an iron removal stage as detailed in this chapter. The primary and secondary leaching sequence is illustrated in Figure 5.1.

It was not until the development in the late 1960s of suitable methods of separation of significant amounts of iron from solution in a form which could be readily filtered and washed, that secondary leaching of zinc ferrite (or primary leach residues) was practical. Such iron separation methods were the jarosite, goethite and hematite processes that are detailed below. Prior to the development of those processes the only precipitation method available for iron was simple neutralisation to give ferric hydroxide. This precipitate is gelatinous and difficult to separate by settling and filtration. It also tends to entrain large quantities of zinc sulfate and therefore contributes little advantage to the leaching of zinc ferrites. Consequently it is only useful for separation of small quantities of iron, limited to about 2 g/L.

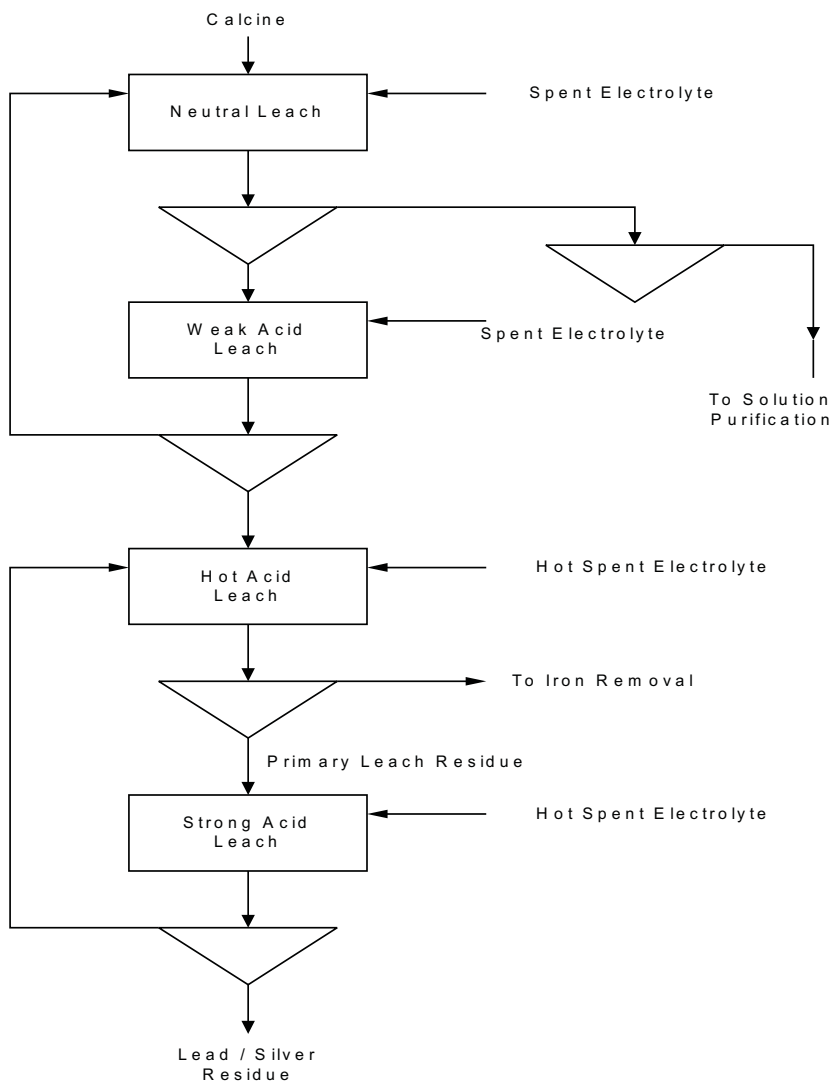


FIG 5.1 - Primary and secondary leaching flow sheets.

There are many variants of the generalised flow sheet given in Figure 5.1, depending on the nature and grade of the calcine processed, the presence of critical impurities and the method of integration with the iron removal stage. Recovery of a lead-silver residue is also a key issue in flow sheet design and may not be justified if lead and silver values in the concentrate are low. In that case, hot acid leach pulp may flow directly to the iron removal stage without solids separation, and leaching and iron separation may be closely integrated.

Primary Leaching

Neutral leaching will dissolve any zinc sulfate and basic zinc sulfates as well as a significant proportion of the zinc oxide content in accordance with Equation 5.1.

At pH levels above five, there is potential to form basic zinc sulfate according to Equation 5.2.



The equilibrium position is controlled by the concentration of zinc and sulfate and the solution pH, but zinc can remain in solution up to a pH range of between 4.8 and 6.0. At higher pH levels, zinc hydroxide will form according to Equation 5.3.



The hydroxide is stable in solutions with a pH range of six to seven. At higher pH levels the hydroxide will redissolve and form a zincate ion ZnO_2^{2-} .

In normal practice the pH at which basic zinc sulfate will begin to appear is normally around 5.1. The operating pH range through a series of neutral leach tanks is commonly 4.2 rising to 5.0 to 5.2. A residence time for the neutral leach stage is normally of the order of five hours and depending on the reactivity of the calcine will give a zinc extraction from zinc oxide of the order of 70 per cent.

The weak acid leach commonly operates in the pH range of 2.5 to 3.5 and will extend the extraction of zinc from zinc oxide, but this will depend critically on operating pH levels. In usual circumstances, where the flow sheet incorporates a secondary leaching stage, the degree of zinc extraction from free zinc oxide is not critical and may be of the order of 85 per cent. However, if the iron levels in feed are low the flow sheet may not include a secondary leaching stage, in which case higher acidities may be used within the Weak Acid Leach to maximise the zinc extraction from oxide.

Any iron present in the zinc oxide lattice (derived from marmatitic iron) will be dissolved in the weak acid leach as ferrous iron.

The weak acid leach will also dissolve zinc silicates according to Equation 5.4.



Orthosilicic acid is unstable in aqueous solution and decomposes according to Equation 5.5. That stability is a function of solution pH and orthosilicic acid is highly unstable in extreme ranges of acidity or alkalinity. Maximum stability is usually encountered in the range of pH 3 to 3.5.



Silica precipitates from solution as a polymer, and according to conditions of pH, temperature and dissolved silica concentration, can form either pseudo-crystalline material or highly hydrated gels. If gel formation occurs the separation of leach residues by settling and filtration will become difficult, and as a consequence, the selection of leaching conditions to avoid this situation can be of critical importance. Silica will precipitate under neutral leach conditions and care must be taken to limit the level of soluble silica contained in input solution to that stage. Generally most standard primary leach circuits can handle silica if its level in calcine is below 2.5 per cent. Above this level special flow sheet requirements are usually needed.

Silica precipitation in a condensed or pseudo-crystalline form is favoured by low precipitation rates requiring low concentrations of silica in solution and by certain pH ranges. An insight into the stability of silica in solution is given in Figure 5.2 (Wood, 1963), which shows the stability in solution, expressed as the log of the time taken for the solution to form a gel (as indicated by viscosity), in relation to solution pH. In this case, maximum stability (corresponding with maximum gel time) occurs around pH 2 and minimum stability occurs under strong acid conditions or at a pH of around five to six.

Silica stability can also be influenced by the species in solution, such as the presence of ferric iron and aluminium ions, which aid precipitation, and the presence of fluorine, which can promote gelation.

If solutions containing relatively high and stable concentrations of silica are produced under certain leaching conditions (such as weak acid leaching), then it is important to take care with sharp changes in conditions promoting gel formation (such as the addition of these solutions to the neutral leach stage). Where it is necessary to precipitate silica from such solutions, then in order to promote formation of a more crystalline silica and avoid gelation, it is necessary to ensure sufficient dilution to hold silica at low levels in solution for the precipitation reaction. This will favour the use of large single stage reaction tanks rather than multistage operation for silica precipitation, or for combined zinc silicate dissolution and silica precipitation if operating in an unstable regime.

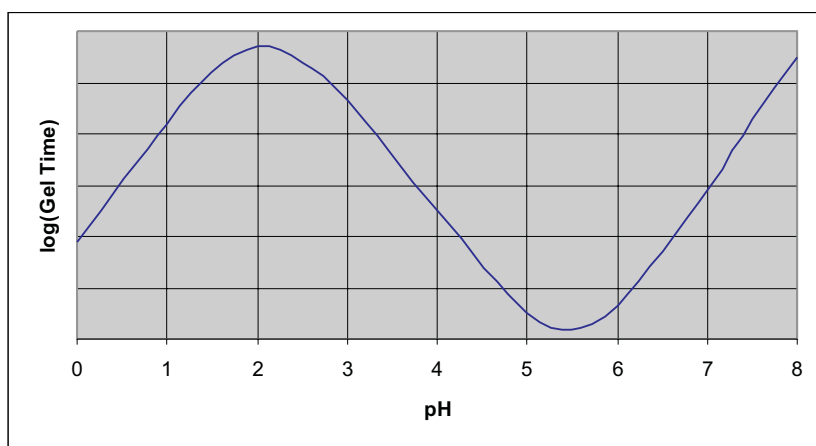


FIG 5.2 - Stability of silica in solution (Fugelberg and Poijarvi, 1979).

Residual quantities of iron from primary leaching and from subsequent operations are also precipitated in the neutral leach as hydrated ferric hydroxide. Since virtually all the iron present in liquors entering the neutral leach stage is in the ferrous form, provision must be made for oxidation which is usually by sparging air into the leach tanks, but can also be by the addition of manganese dioxide in the form of recycled anode sludges. The latter procedure can only be used where manganese input in concentrates is relatively low and this additional input can be tolerated. The origin of ferrous iron in solution flowing back to neutral leach from secondary leaching operations is from the reduction of ferric iron in the hot acid leaching stage by residual sulfides contained in calcine. As a result, the level of iron in return solution to neutral leach will be influenced by the residual sulfide-sulfur content of calcine and will impose practical limits, generally around 0.5 per cent. Residual sulfide will also contribute to zinc losses in residues and needs to be limited for this reason as well.

The precipitation of iron and indeed silica in the neutral leach stage is an important purification procedure not only for the removal of those elements but also for the scavenging of minor impurity elements such as arsenic, antimony, aluminium, indium, gallium, and germanium which coprecipitate, are adsorbed, or form associated compounds such as ferric arsenate. This aspect of the neutral leach stage is most important in terms of achieving satisfactory electrolyte quality and requires good pH control of the leaching operation. As a consequence, a minimal level of iron is needed in solution feed to neutral leach, but also should not be excessive and the target level is generally around 0.5 g/L.

Residual levels of iron contained in neutral leach solution, which proceeds through purification to electrolysis, should be less than 10 mg/L and preferably less than 5 mg/L. This is a particularly important issue for the preparation of high quality solution for electrolysis. The situation can arise where soluble iron levels are relatively low but solids are carried forward due to inadequate clarification of the neutral leach solution before transfer to the purification stage. Because of the high solution

volumes handled, the total solution flow is rarely filtered at this stage but is normally clarified in a large thickener. Poor operation of the thickener-clarifier will allow some solids carryover. The importance of carryover of iron solids is not only the transfer of iron to the electrolyte, but is also the potential for transfer of minor impurities contained in the ferric hydroxide precipitated in the neutral leach stage.

The neutral leaching operation may be conducted in a batch or continuous mode. In the batch leach, calcine and solution will be simultaneously added to a tank with control to a low pH, which is then raised at the end of the leach by calcine addition. Continuous leaching is generally preferred. It is easier to maintain steady leaching conditions and requires less operator supervision. A series of agitated tanks are used, usually fitted with air sparging. The pH in the early tanks is controlled closer to 4.0 but is raised to a final end point of around 5.2. After settling and separation of the leach residue, the clear leach solution may be acidified to reduce the pH to around 4.5 to prevent the precipitation of basic zinc sulfate which contributes to the formation of scale in process equipment.

The weak acid leach stage commonly operates within a pH range of 2.5 to 3.5, but for flow sheets without secondary leaching the acidity can range from five to 10 g/L sulfuric acid in the initial tanks with adjustment to an end point pH of around 3.5 in the final tank. This can cause the re-solution of some impurity elements precipitated in neutral leach and thus give rise to a circulating load within neutral leach and weak acid leach. To achieve the required composition of neutral leach solution this fact may, in some situations, limit the conditions in the weak acid leach.

To enable higher acidities to be used, and as an alternative in the situation where a primary leach only is warranted, a weak acid leach followed by a solution neutralisation and iron precipitation stage can be used. In this case the weak acid leach may operate at an acidity of five to 10 g/L. Solution from the weak acid leach is then neutralised with either limestone or calcine to a pH of around 5.0 to 5.5 and precipitates iron as ferric hydroxide. Air sparging to ensure iron oxidation is necessary. The disadvantage of this approach is the difficulty of settling and filtration of the separate iron hydroxide precipitate, and particularly large filter areas are required. This approach was used in the early designs of electrolytic zinc plant flow sheets but was superseded by the neutral leach-weak acid leach sequence which was termed the 'reverse leach' at the time (Wood, 1963).

The leach residue from a simple primary leach and separated from the weak acid leach stage, contains residual zinc mainly in the form of ferrites with some residual sulfides. It also contains gangue minerals and lead in the form of lead sulfate and includes precious metals. The proportion of zinc remaining in the leach residue or recovery of zinc in the primary leach is determined by the iron content of concentrate used and typical figures are as shown in Table 5.1.

Table 5.1 indicates that the zinc extraction from a primary leach has a significant dependence on the iron content of the concentrate. High iron concentrates result in relatively low zinc recoveries in the primary leach. However, the zinc content of the leach residue does not vary greatly with the iron content of the concentrate. There will be some dependence on the content of gangue minerals but typically primary leach residue contains close to 22 per cent zinc. It is the relative quantity of residue that varies with the iron content of concentrates as shown in Table 5.1.

TABLE 5.1
Primary leach zinc recovery and residue composition.

Zinc in concentrate %	Iron in concentrate %	Zinc Recovery %	Zinc in Primary Leach Residue %	Primary residue amount % of concentrate
48	12	82.8	22.8	36
50	10	85.6	22.8	32
52	8	88.3	22.5	28
54	6	90.7	21.7	24
56	4	92.9	20.9	19

The primary leach residue may be separated and processed via a pyrometallurgical route, which generally involves fuming of the zinc to produce a zinc oxide fume for return to the leaching circuit. This was a common practice prior to development of suitable methods for the precipitation of large quantities of iron from solution. With those developments, aggressive leaching of the primary leach residue to dissolve the ferrites was found to be the most economic approach.

Secondary Leaching of Primary Leach Residue

The zinc ferrites contained in primary leach residue can be successfully dissolved in hot strong sulfuric acid solutions at between 30 and 80 g/L and temperatures of above 90°C. The basic reaction is given in Equation 5.6.



Spent electrolyte is used for leaching and can be heated by heat exchange with steam. This can represent a significant consumption of by-product steam from the roasting plant. Leaching is carried out in a series of agitated tanks to give a total residence time of the order of five hours, often with five tanks in series. These tanks are generally acid brick lined for insulation and corrosion protection. Multiple series tanks are preferred to minimise the impact of possible by-passing of solution.

The acid end point for the hot acid leach is commonly around 30 g/L but can be higher and up to 100 g/L in early stages in the series of tanks. Ferrite extraction is of the order of 80 per cent under these conditions giving iron levels in the resulting leach solution commonly in the range of 30 to 40 g/L. Any residual sulfides contained in leach residues will also be attacked by the ferric iron and extractions of zinc from sulfides will generally be of the order of 50 to 60 per cent, but dependent on the actual amount present.

The secondary leach is often extended to two counter-current stages incorporating a second strong acid leach on residue from the hot acid leach stage. Conditions are a leach temperature above 95°C and a residence time of the order of three hours. This will achieve 90 per cent extraction of ferrites raising the overall extraction in the two stages to above 98 per cent, and will enable the lead content of the final residue to be maximised. It is also important to maintain strong acid conditions to ensure that any jarosites formed during hot acid leaching are re-dissolved (see Iron Removal below). The strong acid leach stage is not always used, but is appropriate if a lead-silver residue is recovered. The lead content of the final residue depends largely on the lead content of the concentrate but can range up to 40 per cent if the strong acid leach is used.

The final residue is settled in a thickener and is filtered usually using a high pressure filter press in preference to vacuum filtration. If the lead and silver contents are suitably high, the residue can be further processed in a lead smelter for recovery of the lead and silver contents. It is generally the silver content that determines the marketability of this material. The hot acid leach solution must be processed for the separation of iron and is then passed to the primary leach stage.

IRON REMOVAL

As indicated above, for the removal of any significant quantities of iron from solution (that is above 2 g/L), it is necessary to precipitate the iron in a form that can be readily settled, filtered and washed with minimum entrainment of leach solution. Processes that have been developed rely on the use of three iron compounds - jarosite, goethite and hematite. The jarosite process has many variants and is probably the most cost efficient removal method. Goethite can be produced in two principle ways, one variant known as the goethite process and the other as the paragoethite process. Hematite can only be produced at elevated temperature and pressure and hence involves treatment of solution in an autoclave.

In all cases, it is necessary to separate the iron precipitate in as coarse a crystalline form as possible to achieve high settling and filtration rates and to reduce solution entrainment. Generally this requires

iron to be precipitated from a low iron concentration in solution in order to minimise nucleation. But in order to promote crystal growth, the addition of seed material in the form of recycle precipitate will clearly assist.

The Jarosite Process

This process was developed in the mid 1960s and represented a most significant advance in the electrolytic zinc process (Arregui, Gordon and Steintviet, 1980).

Jarosite is a complex basic iron sulfate represented as $R_2Fe_6(OH)_{12}(SO_4)_4$ where R may be any of the ions K^+ , NH_4^+ , Na^+ , Ag^+ , or R_2 can be Pb^{2+} . Solution temperatures close to the boiling point are required for the formation of jarosites, and formation is favoured at lower solution acidities. The stability of the jarosite compound roughly follows the above series with potassium jarosite being the most stable. It can be precipitated at lower iron levels and at higher acidities. The lead form or plumbojarosite, generally requires elevated temperatures to form and usually only appears in autoclave residues.

Potassium and sodium are always present to some extent in concentrates and hence their jarosites are invariably formed from high temperature leach solutions containing iron. However there is far from sufficient amounts to precipitate all the iron leached from ferrites and it has generally been found that ammonium is the lowest cost reagent for precipitation of the bulk of the iron as jarosite. Due to the lower stability of ammonium jarosites there will be significant levels of ammonium ion in the electrolyte, typically of the order of 3 g/L, whereas residual levels of sodium and potassium are each of the order of 0.3 g/L.

The reactions for ammonium jarosite formation are given in Equation 5.7.



For every mole of iron precipitated as jarosite, one mole of sulfuric acid is formed. In order to allow the precipitation reaction to proceed, neutralisation of the acid formed is necessary. The addition of ammonia rather than ammonium sulfate will assist, but additional neutralisation is required and this is generally achieved by the addition of calcine. The equilibrium level of iron in solution is largely dependent on the acid concentration and the rate of precipitation is highly dependent on temperature. The relationship between these parameters as reported in the literature varies considerably, with some data indicating a linear relationship as a practical guide for mixed jarosite precipitation. In this case at a temperature of around 95°C the residual ferric iron in solution in g/L is equal to 0.2 times the sulfuric acid concentration in g/L. This is a rough guide up to a level of around 120 g/L H_2SO_4 . Thereafter the iron concentration rises sharply (Huggare, Fugelberg and Rastas, 1974). For a more extensive range of conditions it has also been proposed that the ferric iron concentration is proportional to the square of the acid concentration (Matthew, Haigh and Pammenter, 1983).

The equilibrium solution concentration ratio (in g/L) of Fe^{3+} : $(Acid)^2$ for jarosite precipitation at 95°C has been given as:

Ammonium jarosite precipitation	0.004
Potassium jarosite precipitation	0.002
But for practical precipitation rates a suitable operating ratio is	0.010

The zinc ferrite associated with the calcine used for neutralisation is largely unreacted by the acidity conditions of ten to 15 g/L and the residence times of around six hours normally used for jarosite precipitation, and constitutes a loss of zinc with the jarosite residue. In order to reduce this zinc loss and the quantity of calcine used for jarosite precipitation, it is common practice to use a pre-neutralisation step, including thickener, ahead of jarosite precipitation. This aims to reduce residual acidity in hot acid leach solution to a low level in a separate stage from which the residue can be separated for subsequent

treatment in the hot acid leach stage with recovery of the ferritic zinc. Acidity is reduced to the point where jarosite just commences to form. Also, reducing the operating temperature, even to 85°C, can greatly assist in preventing jarosite precipitation at lower acidity levels. In this way, the acidity of hot acid leach solutions at around 30 g/L H_2SO_4 can be reduced to between five and 10 g/L prior to jarosite precipitation.

Another means of reducing zinc losses associated with zinc ferrite contained in the jarosite residue, is to subject the residue to an acid re-leach. This is possible because, once formed, jarosite has a higher stability in acid solution than zinc ferrite and is subject to only limited re-solution. For re-solution of jarosite to occur, much higher acidities than used in precipitation are needed, and a practical ratio of ferric iron: (acid)² of 0.002 (concentrations in g/L) may be required to ensure that all ammonium jarosite is re-dissolved (Matthew, Haigh and Pammenter, 1984). If acidities are held below the critical level indicated by this ratio, ferrites can be dissolved without significant re-solution of jarosite. These conditions are also relevant for the strong acid leach stage if all jarosites, which may have formed during hot acid leaching are to be removed. In that case higher acidities than indicated by the above ratio are needed. A generalised form of jarosite precipitation flow sheet is given in Figure 5.3

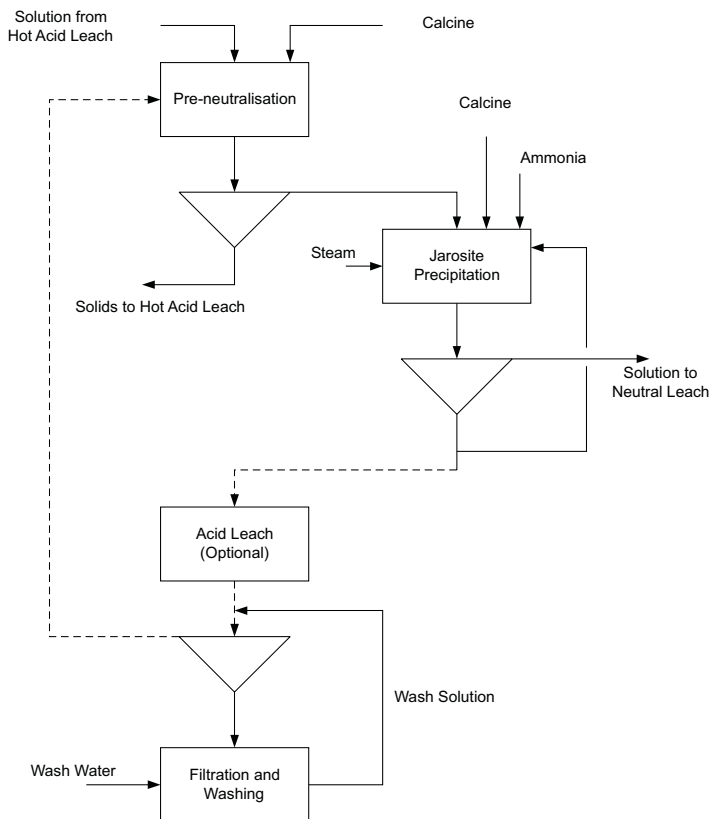


FIG 5.3 - Typical jarosite process flow sheet.

Operating temperatures for jarosite precipitation are generally above 90°C, acidity can be of the order of 10 g/L and iron levels are generally reduced to less than 5 g/L. The residual iron is eventually removed from solution in the neutral leach stage, where it is diluted by direct spent electrolyte additions to the neutral leach and precipitated as ferric hydroxide. This iron which reports to primary leach residue will be redissolved in the hot acid leach and thus forms a circulating load, but allowing all dissolved iron to exit the leach circuit as jarosite.

As indicated above, the precipitation of jarosite at low iron levels requires time for induction or nucleation as well as time for crystal growth. The operation can therefore be significantly enhanced by the recycle of jarosite solids to the first precipitation tank to act as seed. Typical residence times for jarosite precipitation are six hours using multiple tanks in series, usually of around one hour residence time per tank.

The high degree of dependence on high solution temperatures for jarosite precipitation was utilised in a patent by the EZ Company of Australasia Limited (Pammenter and Haigh, 1984) in which the hot acid leach solution was cooled and neutralised to an excessive extent such that complex ions of the form $\text{Fe}(\text{OH})_4^-$ were formed in solution and allowed for subsequent jarosite precipitation simply by heating the resulting solution without the need for addition of a neutralising agent. This resulted in a relatively 'clean' jarosite with high zinc recovery.

Other variants of the jarosite process have aimed at reducing the quantities of ferrites retained in the jarosite residue, and two notable procedures are the Dor Variant and the Outokumpu Conversion Process.

The Dor Variant of the jarosite process was used for many years at the Budel smelter in the Netherlands and is shown in Figure 5.4.

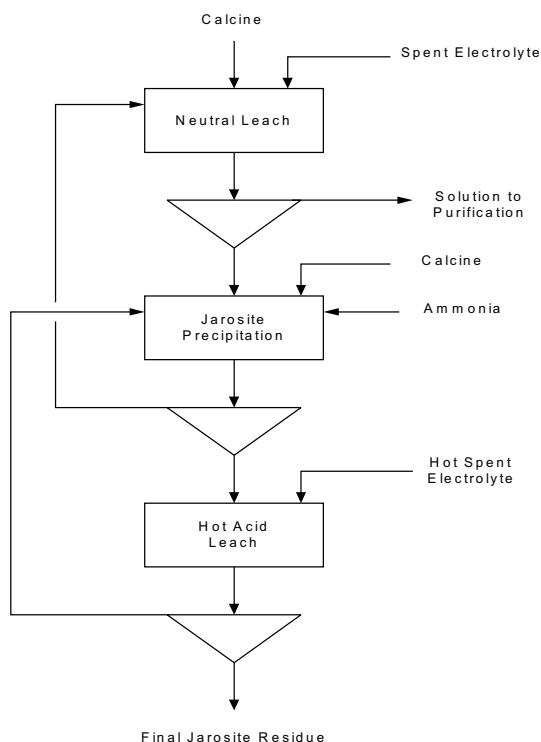


FIG 5.4 - Dor variant of the jarosite process.

The Dor Variant process re-leaches the jarosite precipitate after separation, with strong acid solution to attack and dissolve the contained ferrites and relies on the fact that the jarosite precipitate itself is slow and difficult to re-dissolve in sulfuric acid, as discussed above. In this situation it is possible to combine the jarosite re-leach and the hot acid leach stages with primary leach residue as well as calcine being used as the neutralising agent for jarosite precipitation. This gives a very simple and manageable flow sheet as shown in Figure 5.4, but does not allow for the separation of a lead-silver residue.

The Outokumpu Conversion Process combines the hot acid leach and jarosite precipitation stages using zinc ferrite as the neutralising agent and effectively results in the conversion of zinc ferrite into jarosite within the one operation. The acid liberated by jarosite formation according to Equation 5.7 can be used in leaching of the ferrites according to Equation 5.6 and, as a result, half the acid addition is needed than if ferrite leaching were conducted separately. However, because of the relatively low acidity requirements for jarosite precipitation, attack on ferrites is slow and extended residence times and hence large tankage volumes are required. To some degree, this is compensated by reduced acid inputs and solution flows. This procedure was developed by Outokumpu at the Kokkola smelter in Finland and is in use in other plants such as the Valleyfield smelter of Canadian Electrolytic Zinc (Rosoto and Berube, 1993). Again this flow sheet is simple as shown in Figure 5.5 but does not allow for separation of a lead silver residue.

The composition of jarosite residue depends to some extent on the flow sheet used, the separation of a lead-silver residue, and the level of ferrite residues retained in the jarosite residue. By formula, potassium jarosite contains 33.5 per cent Fe, and ammonium jarosite contains 34.9 per cent Fe. In practice, typical jarosite residues contain 29 to 30 per cent Fe and around five per cent Zn. The zinc arises largely from undissolved ferrites from the calcine used for jarosite precipitation.

One important consequence of the jarosite process is that it provides an outlet for sulfate from the closed solution circuit. There is some addition from the sulfate content of calcine but this is insufficient to balance the loss and sulfuric acid must be added to maintain the circuit sulfate balance. This addition can be used to advantage by raising leach solution acidities in the strong acid leach and hot acid leach stages, above that provided by spent electrolyte alone. This will allow for reduced solution flows and reduced equipment sizing.

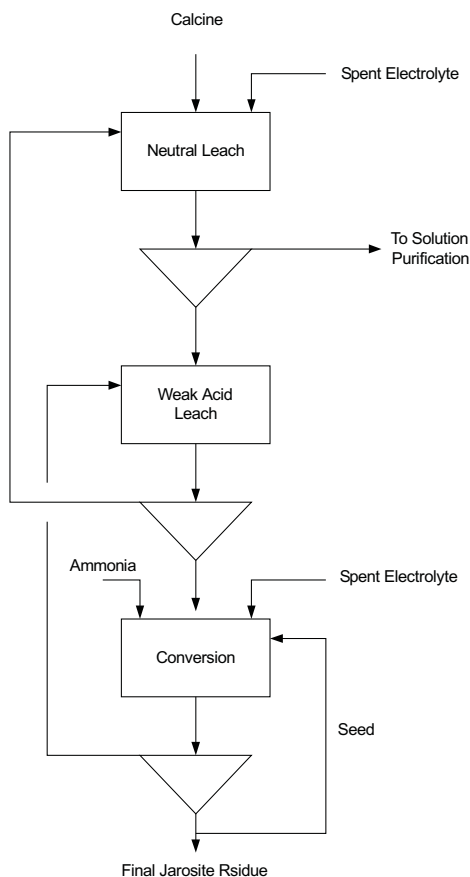


FIG 5.5 - Outokumpu conversion variation to the jarosite process.

The Goethite Process

The phase diagram for the system $\text{Fe-SO}_4\text{-H}_2\text{O}$ is shown in Figure 5.6 (von Ropenack, 1998). This indicates that at high ferric iron concentrations the stable equilibrium solid phase is 'hydronium jarosite'. At intermediate ferric iron concentrations (above 2 g/L and less than 12 g/L), the stable phase is an amorphous basic sulfate, and below 2 g/L Fe the stable solid phase will be hydrated ferric oxide or goethite. The highly basic sulfate in particular tends to be gelatinous and difficult to settle and filter, whereas goethite is relatively crystalline and has good settling and filtration properties. If this is to be used as a technique for removal of iron from solution in a manageable form, then it is necessary to maintain the concentration of ferric iron in solution below two or preferably 1 g/L during precipitation.

Given that the level of ferric iron in ferrite leach solutions is of the order of 30 g/L, two procedures are used for maintaining iron levels below 2 g/L:

1. The iron is reduced to the ferrous state using zinc sulfide concentrates, and is then re-oxidised with air in the goethite precipitation tanks such that the ferric iron concentration is maintained at a low level. This is the basis of the goethite process developed by Vieille Montagne at the Balen smelter (Andre and Masson, 1973; and Bellefroid, 1985).
2. If the high ferric iron solution is fed slowly to the precipitation tanks in a continuous system, the level of iron in the tank can be maintained at a suitably low level. This of course means that the precipitation must be carried out in a single stage rather than a series of tanks. This approach was developed by the Electrolytic Zinc Company of Australasia as the EZ Ferric Oxide Process and is generally referred to as the paragoethite process (Patrizi, Persia and Pescetelli, 1985).

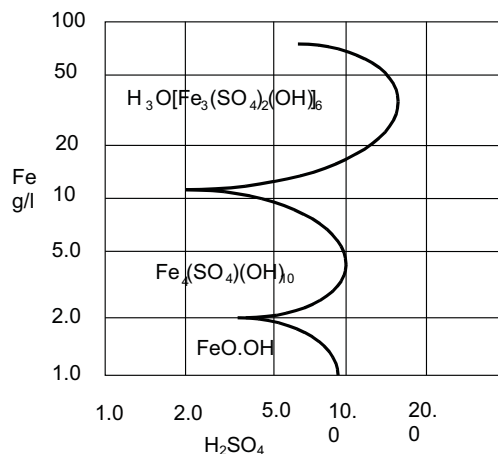


FIG 5.6 - Fe – SO₄ – H₂O system at 100°C (von Ropenack, 1990).

The VM Goethite Process

As indicated above, the first step in this process is to reduce the solution arising from the leaching of ferrites with concentrates according to the following equation:



The residue from the reduction step contains elemental sulfur as well as unreacted sulfides, and is separated and returned to the roasting plant.

The resulting solution containing ferrous iron is then re-oxidised to ferric iron using air, and goethite is simultaneously precipitated according to Equation 5.9.



Acid is generated as in jarosite formation and calcine is added to neutralise that acid and maintain the required operating pH. A pH above two is necessary for air oxidation of ferrous iron and a range between 3.5 and 4.0 is generally preferred. Operating temperature is around 95°C as for the jarosite process. A typical flow sheet for the VM goethite process is given in Figure 5.7.

In the VM goethite process, as shown by Equation 5.9, one mole of acid per mole of iron precipitated is formed and must be neutralised, which is the same as for jarosite precipitation (Equation 5.7). Hence the losses of zinc associated with ferrites are theoretically similar for both processes, but are higher for the goethite process due to the lower efficiency in the use of calcine at the lower acidities. Goethite is also less stable than jarosite and can redissolve if the acidity is raised. Hence the opportunity to recover excess zinc, lost as ferrite by an acid re-leach, is not available and zinc losses are significantly higher than for the jarosite process.

The formula iron content of goethite is 62.9 per cent. However, due to the uncertain degree of hydration, the presence of other entrained salts and the calcine residues the practical iron content is

reduced to the range of 40 to 43 per cent. Even so, this is significantly greater than the content of jarosite at 30 per cent Fe, hence the quantity of iron residue is less than 75 per cent of that derived from the jarosite process. Because of the higher zinc losses, goethite tends to contain zinc at eight to ten per cent in comparison with jarosite at three to five per cent. Even accounting for the reduced quantity of residue, zinc losses for the goethite process are thus significantly higher than for the jarosite process.

Although both jarosite and goethite appear to act as scavengers for the removal of minor impurities such as As(V), Sb(III and V), In, Tl, and F, goethite may be more effective in this regard.

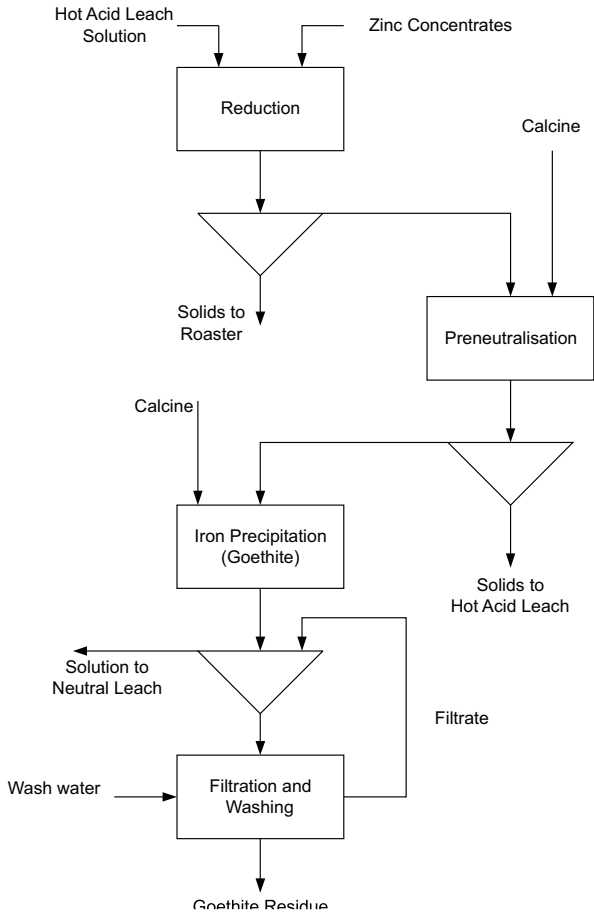
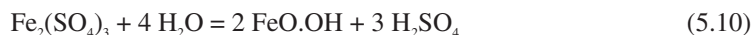


FIG 5.7 - VM goethite process flow sheet.

The Paragoethite Process

In this case, the low ferric iron concentration necessary for the formation of the goethite structure is achieved by control of the solution flow to the precipitation tanks. It is generally necessary to carry out the precipitation operation in a single stage rather than a series of tanks where there would be a gradation in iron concentration. Hence, very large tanks or a number of single stage tanks operating in parallel are generally used. In this situation it is particularly difficult to ensure concentration uniformity and the maintenance of ferric iron concentration below 2 g/L at all times. As a result, the form of iron precipitate is not pure goethite but contains hydrated basic sulfate, has poor crystallinity and contains a higher level of entrained zinc than the pure goethite product.

The precipitation reaction is ideally according to Equation 5.10.



In this case, 1.5 moles of sulfuric acid are produced per mole of iron precipitated, which is 50 per cent higher than for the VM-goethite process and hence requires 50 per cent more calcine for neutralisation, correspondingly increasing the losses of zinc as ferrite. A typical flow sheet is shown in Figure 5.8.

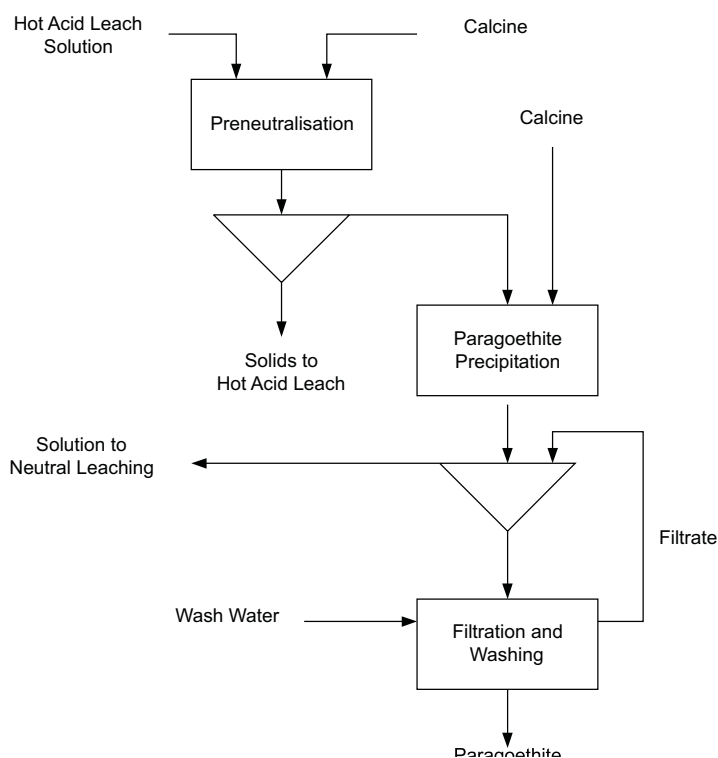


FIG 5.8 - Paragoethite process – general flow sheet.

Although the paragoethite process simplifies the flow sheet by eliminating the iron reduction stage, it does so at the expense of increased quantities of iron residue and increased zinc losses with lower overall zinc recovery from concentrates. The process is more difficult to control to achieve satisfactory settling and filtration properties and to maintain low levels of entrained zinc in the final residue.

The paragoethite residue is typically 33 to 35 per cent Fe with a zinc content of ten to 15 per cent.

In situations where the iron residues are further processed by pyrometallurgical methods to recover metal values, the higher zinc content may not be such an issue as in the case where the iron residue is sent to disposal ponds. However, the process simplifications of the paragoethite process must be balanced against further residue processing costs. This approach has been used at the electrolytic zinc plant of the Porto Vesme smelter in Sardinia where paragoethite residues are treated in a Waelz kiln, and at the Hobart smelter of Zinifex Limited where residues are sent to an associated lead smelter that incorporates zinc recovery by slag fuming.

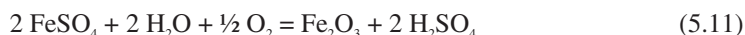
This approach can also be useful in the case of low iron content concentrate feeds where the quantities of iron residue are in any event relatively low.

The Hematite Process

The equilibrium solid phases in the Fe - SO₄ - H₂O system change at elevated temperature and are significantly less hydrated. This is illustrated in Figure 5.9 (von Ropenack, 1990), for a temperature of 175°C.

Iron may be precipitated from solutions containing higher acid concentrations, and at lower final ferric iron concentrations hematite (Fe₂O₃) rather than goethite (FeO.OH) is the stable phase. At higher concentrations, the stable phase is the basic iron sulfate FeSO₄(OH).

In the hematite process, the feed solution is generally reduced as in the VM goethite process to convert all iron to the ferrous state. The solution is heated to between 180 and 200°C in an autoclave with the addition of oxygen. As a result, ferric iron concentrations can be maintained at a low level ensuring that pure hematite is formed, and acid generation is minimised. The precipitation reaction is as follows:



The acidity is generally allowed to rise to the equilibrium level, which to some extent imposes practical limits on the iron concentration in solution feed to the autoclave. However a particularly high grade iron residue can be produced relatively free of zinc.

The iron content of hematite produced in this way is typically 55 to 60 per cent and the zinc content is around one per cent, with 1.5 per cent S. Being free of zinc ferrite residues, in contrast to other iron removal processes, and being inherently low in zinc content, the overall smelter zinc recoveries achieved by use of the hematite process are very high and can exceed 99 per cent from concentrates. The volume of iron residue produced is also much lower at less than half the quantity produced by the jarosite process.

Early development objectives of this process were to produce a hematite of sufficient purity for use as feed for iron production. The process has been operated at the Datteln plant of Ruhr Zinc in Germany and at the Iijima plant of the Akita Zinc Co in Japan. In both cases the impurity levels (particularly zinc and arsenic), were too high for acceptance by the iron and steel industry. Some of the hematite was acceptable as a feed component for cement manufacture but this outlet is limited and other disposal routes were also necessary. Due to the high cost of this process relative to goethite and jarosite processes, the Ruhr Zinc operation ceased in 1993.

In the Akita Zinc flow sheet, the primary leach residue is leached with spent electrolyte and sulfur dioxide in an autoclave at 100°C and at a total pressure of 21 bar. This step dissolves the ferrites and leaves the iron in the ferrous state. The resulting solution is treated with H₂S or finely ground zinc concentrate to precipitate copper, and is then neutralised with lime to pH 4.5 to separate minor impurities such as gallium, germanium, arsenic, and antimony. The resulting solution then passes to the hematite precipitation autoclaves (Yamada, Kuramochi, Sato and Shibasi, 1998).

At the Datteln plant, ferrite residues were leached using conventional hot acid leach and strong acid leach stages followed by reduction of iron to the ferrous state with concentrates. Hematite was

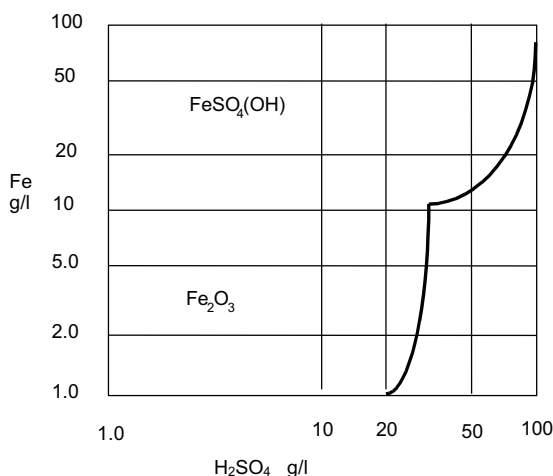


FIG 5.9 - Fe - SO₄ - H₂O system at 175°C (von Ropenack, 1990).

precipitated in an autoclave at 200°C and an oxygen partial pressure of five bar and total pressure of 20 bar.

One feature of operating hematite autoclaves can be the tendency for deposition on the walls of the vessel and the need for significant downtime for cleaning. This can necessitate the need for multiple units to allow for continuous operation and can significantly raise the capital cost of the plant.

Union Minière piloted a high-pressure pipe reactor as a lower cost alternative to a conventional autoclave (Torfs and Vliegen, 1996). However, blockage due to wall deposits was a problem and it was concluded that the process was not competitive.

The hematite process has significant advantages in terms of high smelter zinc recovery from concentrates and a minimum quantity of iron residue. However, if there is a need to dispose of the iron residue and if there are no associated by-product credits from the hematite, then the cost of the hematite process does not compare favourably with other iron removal methods.

Comparison of Iron Removal Processes

The various iron removal processes outlined above result in significantly different quantities of residue and loss of zinc, as well as different equipment and operating costs. Selection of the most suitable process will depend to a large extent on the options available for residue disposal, and the primary issue may be the quantity of residue produced rather than zinc recovery achieved. The choice of process also impacts on the quantity of secondary leach (or lead–silver) residue produced due to the difference in the quantity of calcine used for iron precipitation. The residue normally associated with that calcine will be incorporated into the iron residue.

Table 5.2 compares the four principal iron removal processes in terms of residue tonnage and zinc recovery for a typical zinc concentrate feed containing 52 per cent Zn, two per cent Pb and seven per cent Fe, and assuming a secondary leach residue composition of 25 per cent Pb, eight per cent Fe and five per cent Zn.

TABLE 5.2
Comparison of iron removal processes (based on 100 tonne of zinc concentrate feed).

Process	Jarosite	VM-goethite	Paragoethite	Hematite
Iron Residue				
Fe content	29.0%	40.0%	34.0%	57.0%
Zn content	3.5%	8.5%	13.0%	1.0%
Pb content	1.9%	1.9%	2.2%	0%
Quantity of Fe residue	22.5 t	16.2 t	19.2 t	11.2 t
Zinc loss in Fe residue	1.51%	2.65%	4.79%	0.21%
Quantity of sec leach residue	6.0 t	6.5 t	6.0 t	8.0 t
Zinc loss in sec leach residue	0.58%	0.63%	0.58%	0.77%
Overall zinc recovery	97.9%	96.7%	94.6%	99.0%

Other Iron Removal Techniques

Removal of iron from solution by selective solvent extraction has been investigated and proposed in various forms. Both versatic acid and D2EHPA have been considered for this application. However, issues such as the relatively low loading of the solvents, the introduction of organics that can impact on electrolysis unless precautions are taken, the cost of reagents and their loss, and the need to ultimately precipitate iron in a disposable form, all detract from practical application in comparison with direct precipitation methods.

LEAD-SILVER RESIDUE RECOVERY

Justification for the recovery of a lead-silver residue depends on the levels of both lead and silver contained in feed concentrates. Recovery can add to flow sheet complexity and if these elements are low then recovery may not be economically viable. However, recovery can be required for environmental reasons to reduce the level of base metals contained in disposable iron residue.

Recovery is essentially as a residue containing the insoluble gangue minerals from the original concentrate plus lead sulfate containing silver. The most common approach for recovery is as the final residue after the strong acid leach. This can yield a material containing up to 45 per cent lead and is usually sold to a primary lead smelter where it is incorporated into smelter feed with lead concentrates. For the conventional lead smelter using sinter plant and blast furnace technology, this involves incorporation into the sinter plant charge. Due to the endothermic reactions involved with sintering lead sulfates and the potential for adverse impacts of fine sludges on sinter bed permeability, the proportion that can be added to the sinter charge is limited. Consequently, the outlet for lead sulfate residues by this route is limited and commercial terms for the sale of the residue are poor. Alternative direct lead smelting processes such as the Kivcet and QSL processes do not have the same restrictions and can accept greater quantities of lead sulfate residues. However, this does raise fuel costs and displaces high grade lead concentrate feed, and can reduce overall smelter production. Hence there are penalties for the treatment of such materials.

Other options are electric furnace treatment but commercial applications are very limited. In general terms, the value of lead recovered from these residues barely covers the freight from the zinc smelter to the lead smelter and the processing costs, and any value gained is largely realised from the silver content and sometimes gold.

Because of these complications, another approach that is employed by a number of electrolytic zinc plants is to minimise the quantity of residue and at the same time maximise the silver content. This is done by use of flotation after sulfidisation of the residue with sodium sulfide to produce a lead concentrate rich in silver. The recovery of lead may not be high but generally the recovery of silver can exceed 90 per cent, and a valuable high grade material can be produced, which is far more marketable as feed to lead smelters than the total leach residue. This approach can optimise the by-product return from lead and silver even though part of the lead and silver will be lost and probably report to the iron residue.

If pyrometallurgical treatment of the iron residue is available then separation of a lead - silver residue may not be necessary. The exception to this would depend on the actual pyrometallurgical route used and its efficiency in the recovery of silver. The Waelz kiln for instance is poor in this regard, whereas slag bath fuming can give high silver recovery to the zinc oxide fume (see Chapter 16). Clearly many factors need to be taken into account to enable decision of the preferred approach, such as:

- the level of lead and silver contained in the concentrate feed;
- the ability to dispose of iron residues containing lead including environmental regulations for the construction of long term storage facilities;
- access to lead smelting operations;
- available commercial terms for sale of the lead-silver residue;
- the availability of pyrometallurgical processing for zinc plant residues; and
- the recovery of silver in such pyrometallurgical processes.

THICKENING AND FILTRATION OF IRON AND LEACH RESIDUES

The separation of iron and leach residues from solution is a key operation, and because of the variable nature of the solids, can often restrict the throughput of the entire zinc plant. As discussed above, the characteristics of the precipitates formed in various leaching stages, such as iron and silica precipitates,

are of major importance in determining the ease of separation from solution. It is these characteristics that largely determine the conditions used in various leaching stages. Variations in operating parameters such as residence time, temperature, pH and the presence of seed material, as well as changes in calcine composition, can have a significant effect on precipitate properties and hence on the performance of settling and filtration operations. It is therefore prudent and usual to allow some latitude in the design of this equipment to cover possible variations.

To some extent, variations can be compensated by the use of flocculant additions. These materials agglomerate or flocculate fine particles by surface action and 'bridging' into clumps or flocs to enhance settling and filtration properties. The flocculant must be carefully selected for the particular solution conditions and must be added in a suitable manner to ensure optimum floc formation. Generally flocculants must be used in as dilute a solution as possible, and should be introduced into the pulp stream progressively and with gentle mixing. The pulp should not be subjected to excessive shear forces thereafter since the flocs can be broken down and destroyed. The best method of addition is by multi point injection into the feed launder of a thickener. Excessive use of flocculant can provide good solution clarification but low thickener underflow densities with a strong open floc structure holding large quantities of entrained solution.

The first stage of solids separation is usually the thickener followed by filtration of the thickener underflow as the second stage. Recent installations tend towards the use of the 'high rate' thickener for primary duty. In these units, feed flows from the central feed well beneath the pulp layer in the body of the thickener, which acts as a filter bed. Significantly higher rates can be achieved than in the standard thickener operating with a shallow pulp bed. The pulp level should be constantly monitored for control and it is possible to link this with the control of flocculant addition.

It is common practice to have at least two primary thickeners in parallel to allow one to be taken out of service for cleaning without interrupting production. In some situations, it is also common for the overflow from the primary thickeners to flow to a clarifying thickener of standard design and hence of considerably greater area than the high rate primary units. In terms of neutral leach solution, the use of the clarifying thickener is of particular importance in controlling the transfer of iron through to pure solution. The clarifying thickener is only used where minor transfer of a small amount of solids suspended in solution to the next stage must be avoided.

The aim of the primary thickeners is to separate the solids into as dense a form as possible. Selection of the most appropriate flocculant and avoidance of excess is important in achieving maximum underflow density. The underflow pulp is usually pumped by means of variable speed centrifugal pumps to the filters, or to the next processing stage.

Table 5.3 indicates the typical sizing of thickeners for zinc leaching operations.

TABLE 5.3
Typical thickener capacities.

Thickener Type	Area for Solution flow (m ² per m ³ /h)	Area for Solids flow (m ² per t/h)	Underflow solids density (g/L)
High rate - normal	0.4 - 0.8	10 - 15	400
High rate - dilute pulps	0.4 - 0.6	30	400
Standard thickener	1 - 2	30	400
Clarifier	2.5 - 3		

The choice of filters for iron and leach residue processing varies widely. Early plants used vacuum leaf or Moore filters, in which an assembly of vertical leaves connected to a vacuum header was immersed in a vat of pulp and lifted out by crane when the cake had built up to a nominal thickness. The assembly could be placed in a washing vat before discharging the cake over a dump hopper by a compressed air blow.

Later installations, up to the 1980s, tended to use vacuum drum belt filters fitted with washing sprays and commonly also fitted with string discharge for fine solids such as jarosite. Flat belt filters have also been used to a limited extent but are less suited to fine precipitates.

More recent plants have tended to use large automated plate and frame filter presses such as the Lasta filter, fitted with squeeze action compression drying. This uses a hydraulically activated rubber diaphragm to squeeze the cake and eliminate additional water. These units achieve maximum dewatering of the cake and hence minimum loss of zinc in entrained solution. However even with this degree of dewatering, iron residues can have moisture contents of between 20 and 30 per cent.

For iron residues, large horizontal units with vertically hanging plates and frames and automated opening and cloth washing sequences are preferred. For smaller duties, the vertical stack filter press with cloth belt discharge as in the Larox filter design is suitable and is often applied to final leach residues. This type of filter has a much shorter discharge cycle time and is also more productive for shorter total filtration cycles.

All press type filters operate on a batch cycle including the following sequences:

- Primary filtration
- First stage wash
- Second stage wash
- Air blow drying
- Discharge

Compression is used between stages as appropriate.

Filter area requirements typically fall in the range of 20 to 40 m² per t/h of solids filtered.

The use of wash water must be carefully controlled as it represents the major input to the closed solution circuit and is a key part of circuit water balance control. Consequently, the conditions for optimum precipitation of iron to achieve maximum pulp densities in thickener underflows and as final filter cake are most important.

PROCESSING AND DISPOSAL OF LEACH / IRON RESIDUES

Since zinc smelter feeds are mineral concentrates, they contain a host of gangue elements in varying levels depending on the source of the concentrate. Where possible, the zinc smelter should recover these elements as marketable by-products, such as sulfuric acid, lead-silver residue, copper cement, cadmium metal, mercury, nickel and cobalt residues, gypsum, etc. However, there will clearly be a range of other elements for which marketable outlets cannot be found or the amounts present are too low for practical recovery. This group is predominantly represented by iron, silica, aluminium, manganese, arsenic, antimony, and the halides. A range of trace elements such as germanium, thallium and selenium also cannot normally be recovered cost-effectively but need to have an outlet in a disposable leach residue.

Generally the final secondary leach residue, containing lead and silver values, may be reprocessed in a lead smelter and contains some residual gangue materials such as silica. Otherwise, the principal outlet is the iron residue, which also contains many minor and trace elements. The disposal of this residue is a major issue for the electrolytic zinc process and has occupied considerable process development effort over many decades. For example, a zinc plant producing 200 000 t per year of zinc from a typical concentrate containing 52 per cent Zn and seven per cent Fe, will produce iron residue for disposal of the annual tonnages shown in Table 5.4.

TABLE 5.4

Relative iron residue production for 200 000 t/a of zinc.

Iron Removal Process	Tonne per year of Iron Residue
Jarosite Process	88 300
Goethite Process	64 400
Para-goethite Process	78 000
Hematite Process	43 300

Traditionally jarosite and goethite residues have been stored in lined ponds or ‘tailings dams’, but with increasing environmental restriction on the construction and management of these ponds, alternative outlets are required. As indicated under Iron Removal in this chapter, attempts have been made to secure market outlets for iron as hematite but without success, and even if that could be secured there will always be a smaller volume of waste material that must find a disposal outlet. To address this issue, it is necessary to process the residues to render them inert and acceptable for land fill disposal. The term inert means chemically stable over a long period of time and complying with leaching test criteria so as to avoid any contamination of ground waters when placed in land fill. Alternatively, the residues may be processed for conversion into inert materials suitable for use in the construction industry such as concrete aggregate or road base material, both of which can accept substantial tonnages.

Two broad approaches for the processing of residues have been used:

1. chemical processing by blending with other materials so as to alter physical and chemical characteristics; and
2. pyrometallurgical processing, generally involving conversion into an inert slag but also offering the opportunity to recover zinc, lead and silver otherwise lost in the residues.

Chemical Processing

The simplest approach involves the addition of lime and/or cement to the iron residue. This can produce a compact material that can be heaped and stockpiled, thus occupying much less ground area than with pond storage. The material can comply with leaching criteria and can be stockpiled without groundwater contamination. Examples are the Jarofix and Jarochoaux processes (Ek, 1986).

Union Minière developed the Graveliet process in which goethite residue is mixed with blast furnace and BOS converter slags from the steel industry. Reactions between the acidic goethite and basic slags result in a hard inert material after a period of curing. The product is suitable for application as a concrete aggregate (Winters, Vos and Canoo, 2000).

Various techniques exist for the chemical decomposition of jarosite such as heating in an autoclave at 200°C with reaction according to Equation 5.12



For the reaction to proceed completely it is necessary to also introduce a neutralising agent, such as ZnO or ferrite residue ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$), to consume the acid generated

In a similar way, jarosite can be decomposed using ammonia but produces significant amounts of ammonium sulfate.

Thermal decomposition by roasting at around 1000°C is also possible but is energy intensive. If applied to sodium or potassium jarosite, these reagents can be recovered by leaching their sulfates from the resulting ferric oxide calcine, but with the danger of also recycling deleterious impurities.

These conversion processes serve to reduce the quantity of residue but do not overcome the basic need for disposal of a contaminated iron oxide residue and add considerable processing cost. As a result, there has been little justification for their adoption.

Pyrometallurgical Treatment of Leach Plant Residues

Prior to the development of processes for the separation of iron from solutions resulting from the leaching of zinc ferrites, the approach used for recovery of the remaining zinc in leach residues was a pyrometallurgical route. The two principle options were treatment in a primary lead smelter coupled with a slag fumer to treat a high zinc content lead blast furnace slag, or direct fuming of zinc from the

residue in a Waelz kiln. In both instances, zinc is recovered as a zinc oxide fume, which can be recycled to the electrolytic zinc plant. Zinc fuming processes are discussed in detail in Chapter 16.

These treatment methods fell from favour after the successful development of processes with the ability to extract residual zinc from ferrites by hydrometallurgical methods using the jarosite and goethite processes. However, due to the increasing environmental restrictions on the disposal of iron residues as land dumps or in storage ponds, these approaches are being reconsidered. In addition, high intensity smelting processes have become available and these can improve the economics of residue treatment. Such processes are:

- direct lead smelting processes such as Kivcet and QSL;
- submerged slag injection processes for fuming zinc and lead such as Ausmelt technology;
- flame reactors for fuming such the Contop cyclone furnace or the Horsehead Resources Flame Reactor;
- electric furnaces or plasma arc furnaces; and
- a cupola furnace to produce a crude iron, a slag, and a zinc oxide fume.

Details of these processes are covered in Chapter 16 and electric furnace methods in Chapter 17. The objectives of these processes as applied to residues from an electrolytic zinc plant are:

- to convert waste components into an inert slag suitable for use as landfill or for use in construction applications; and
- to recover zinc, lead and silver by fuming. The fume can be separately leached in zinc plant spent electrolyte to recover zinc and yield a high grade lead sulfate residue at over 60 per cent lead content.

Examples of these approaches that have been utilised commercially are:

1. The Trail (British Columbia) smelter of Cominco Limited, which is integrated with a lead smelter utilising the Kivcet Process, and which treats a primary leach residue containing 12 per cent Zn.
2. The Hobart smelter of Zinifex Limited, which is integrated with the Port Pirie conventional lead smelter using sinter plant and blast furnace technology. A paragoethite residue containing over 13 per cent zinc is processed in the lead smelter and zinc is recovered as oxide from a conventional slag fumer processing blast furnace slag.
3. The Onsan plant of Korea Zinc, which uses Ausmelt submerged lance slag fuming technology to process a goethite residue.
4. The Porto Vesme smelter (Sardinia) of Eniressor, which processes a paragoethite residue in a Waelz kiln.
5. The cupola or shaft furnace as detailed in Chapter 16 - Fuming in the Shaft Furnace.
6. The Boleslaw Electrolytic Zinc Plant in Poland, which processes primary leach residues in Waelz kilns.

The Waelz kiln is the oldest technique for recovery of zinc by fuming in this context. It utilises a rotary kiln fed with residue and low volatile coal or coke, which constitutes about 25 per cent of the charge mass. Feed composition is adjusted with silica or lime to avoid the formation of low melting point slags, since this will result in excessive stickiness and the rapid build-up of wall accretions, which will block the kiln. Some fuel is fired at the discharge end with counter-current operation. Zinc metal vapour is formed within the charge and volatilises into the gas space where it is oxidised to form a zinc oxide fume. Details of the Waelz kiln process are given in Chapter 16.

There are limits to sulfur in Waelz kiln feed and a prior de-sulfurisation treatment may be necessary, particularly if the residue contains significant amounts of jarosite.

Although both zinc and lead recovery to fume can exceed 90 per cent, silver recovery is poor at around ten per cent and is a significant disadvantage since credits from the fume leach residue can be important by-product credits to off-set the cost of the fuming operation.

In general, the Waelz kiln process has both high capital and operating costs and can be difficult to justify as new equipment. For this reason, many installations have in fact been based on the conversion of an existing kiln from other duties such as lime or cement production (see Chapter 16) (Mattich, Hasselwander, Lemmert and Bezzar, 1998).

High intensity smelting/fuming processes produce a liquid slag from which zinc, lead and silver can be fumed at temperatures of around 1200 to 1300°C using coal as a reductant. The Ausmelt approach utilises two furnaces, each equipped with a submerged lance down which fuel and oxygen enriched air are injected. The residue is melted with partial fuming in the first furnace, which also produces a gas containing sulfur dioxide which must be recovered. Fuming is completed in the second furnace. In both cases, gases are cooled in waste heat boilers and fume is collected using electrostatic precipitators or bag filters (see Chapter 16) (Floyd and Swain, 1998; and Kim, Lee and Lee, 2000).

Lead smelting approaches capture the lead and precious metals as lead bullion and leave the zinc in lead smelter slag, from which it can be recovered using a conventional slag fuming furnace operating at around 1250°C and with coal and in some instances oxygen enriched air injection. Gases are cooled in a waste heat boiler and fume is collected in a bag filter. The disposal of iron residues by this route will require additional fluxing components for the lead smelting operation, such as lime and silica, to balance the iron input and provide the required slag composition. This can reduce lead smelter efficiency and raise costs, and represents the cost penalty of residue processing by this route.

In general, the costs of pyrometallurgical residue processing with fume recovery of zinc are relatively high and can rarely support any input material cost. Hence optimum first pass recovery of zinc in the leaching operation is a sound basic principle, but the degree of recovery targeted will depend very much on particular circumstances.

Fume Leaching

Zinc oxide fume from the above residue processing operations can contain up to 70 per cent Zn depending the lead content. Commonly the fume also concentrates elements such as chlorine, fluorine, arsenic, antimony, and germanium. Separate treatment from the calcine leaching circuit is usually required. Halides may be removed by heating the oxide fume in a kiln for selective vapourisation, or by washing with sodium carbonate solution, which extracts halides without dissolving any zinc. If the fume originates entirely from calcine leach residues, the halide levels will be relatively low except for any input from the fuel used for fuming. In this case, sodium carbonate washing of the fume should be quite adequate.

The de-halogenated fume is then separately leached, using spent zinc electrolyte in a weak acid leach operation. Lead and silver values are recovered as a high grade leach residue. The leach solution is usually dosed with iron, such as by the addition of hot acid leach liquor from the calcine leach circuit, and is then neutralised to precipitate the iron and remove impurities such as arsenic, antimony and germanium. Other special impurity measures may also be necessary. Solution following iron precipitation can be combined with the calcine leach circuit solution at the neutral leach stage.

In developing an appropriate flow sheet for fume leaching it is important to consider the outlets for minor impurities and to avoid developing circulating loads through the residue processing operation. For instance, the use of fume for neutralisation in the calcine leach circuit iron precipitation stage has obvious attractions due to the absence of ferrite residues and the resulting high zinc recovery achieved. However if those iron residues are also recycled to the pyrometallurgical residue processing stage to

produce fume, there will be no outlet for volatile elements such as lead, arsenic and germanium, and circulating loads would continue to increase. If this is the case, then separate fume leaching and solution iron purification as described above, is necessary, with separate disposal of the resulting iron residue (see Chapter 16 - Fume Treatment).

DIRECT LEACHING OF ZINC CONCENTRATES

The direct oxidative leaching of sulfide concentrates under pressure was initially developed by the Sherritt Gordon company and was first applied to zinc concentrates at the Trail smelter (British Columbia) by Cominco Ltd in 1980. That plant, and subsequent installations at the Timmins smelter (Ontario) of Kidd Creek Mines, and the Datteln smelter (Germany) of Ruhr Zinc, were all marginal expansions of existing roast-leach plants. For stand-alone operations and full replacement of the roasting operation, a different set of operating criteria apply, since calcine (or zinc oxide) is not available to complete acid neutralisation. For this application, a two stage counter-current pressure leach has been developed by Sherritt Inc and was installed at the Flin Flon smelter (Manitoba) of the Hudson Bay Mining and Smelting Company.

Direct leaching systems at atmospheric pressure have also been developed and installed as commercial scale pilot operations at a number of smelters. Details of these operations are not readily available.

The Zinc Pressure Leach Process

The zinc pressure leach process (Collins, Doyle, Ozberk and Masters, 1990) involves the direct leaching of zinc sulfide concentrates in sulfuric acid supplied as spent electrolyte, in the presence of oxygen under pressure and at elevated temperatures. The overall reaction is:



In fact the rate of the direct reaction as represented by Equation 5.13 is low. However, it is found that the rate of attack is greatly enhanced by the presence of iron in solution and is dependent on the concentration of ferric iron. This indicates that Equation 5.14 is of most importance.

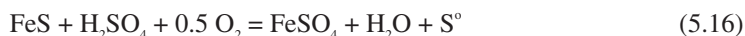


The ferrous iron formed is reoxidised to ferric iron according to Equation 5.15.



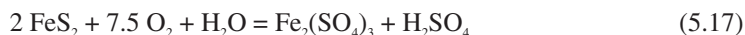
The combination of Equations 5.14 and 5.15 is equivalent to Equation 5.13.

Iron in the form of marmatite or pyrrhotite is normally present in zinc concentrates in sufficient amount to allow these reactions to proceed. In that case the iron is dissolved according to Equation 5.16.



Lead and other metal sulfides react in a similar way to zinc sulfide according to Equation 5.13.

Pyrite is attacked in accordance with Equation 5.17 and results in the formation of sulfate or sulfuric acid rather than elemental sulfur. This will cause a sulfate imbalance to a closed electrolytic zinc circuit and compensating outlets for sulfate need to be provided. However, the reaction is relatively slow and is impeded by operation under acid conditions and at lower oxygen partial pressures. Residence times and conditions can be optimised to minimise pyrite attack and sulfate formation.



To some extent, elemental sulfur can also be oxidised according to Equation 5.18.



This reaction can also be impeded by operation at high acidities. The combination of Equation 5.18 with Equation 5.13 expresses the direct oxidation of zinc sulfide to zinc sulfate. Generally up to five per cent of non-pyritic sulfur can be oxidised to sulfate in this way.

To achieve high rates of reaction under high acid conditions, these reactions are normally conducted at elevated temperatures in an autoclave and leaching is completed within a residence time range of 40 to 120 minutes, depending on the reactivity of the concentrate. The sulfur formed is molten above 120°C and hence at practical autoclave temperatures. Molten sulfur tends to wet and coat metal sulfide surfaces and thus impede the reaction. To counteract this, surface active agents such as calcium lignosulfonate and Quebracho (a wood extract) are added to the leach. It is also desirable to minimise the viscosity of the liquid sulfur, which is lowest between 148 and 158°C. Above 158°C the viscosity rises very rapidly due to sulfur polymerisation, consequently the normal temperature range used for pressure leaching is 145 to 155°C.

Oxygen partial pressure is maintained between 700 and 1200 kPa but is usually at the lower end of the range to reduce equipment costs.

At the optimum operating temperature and at diminishing acidity of the leach solution, iron can precipitate as hydronium jarosite according to Equation 5.19.



Also under these conditions lead and silver can similarly form plumbo- and argento-jarosites which affect the ability to recover these metals from the leach residue. At lower acidities hematite can also be formed.

If recovery of lead and silver is important, it is necessary to maintain high acid levels, generally above 70 g/L. This also allows for high leaching rates and is practical where calcine is available for subsequent neutralisation. In such a case, where pressure leaching is integrated with roast-leach operations, the pressure leaching equipment required, in terms of autoclave volume, is minimised.

The leach autoclave is generally in the form of a five compartment vessel. Each compartment has a separate agitator designed for gas dispersion as well as solids suspension, and also provision for steam injection. Initially, reactions proceed rapidly with up to 75 per cent completion in the first compartment. A typical flow sheet is given in Figure 5.10 for an integrated pressure leach-roast/leach plant.

The autoclave is discharged through let-down valves into a flash chamber producing steam which is used to preheat autoclave feed. Two flash tanks may be preferred, the first operating at about 120°C and the second at close to atmospheric pressure. Slurry from the flash tanks goes to a conditioning tank to allow the sulfur to solidify and change from amorphous to crystalline state. It also allows micropellets of sulfur and unreacted sulfides to form as an aid for subsequent flotation. Slurry from the conditioning tank passes through a hydrocyclone to give an overflow solution which passes to the calcine leaching circuit. Iron levels may be up to 5 g/L and solution should be added to the calcine leach circuit after the hot acid leach stage for iron removal before introduction to the neutral leach stage. By suitable adjustment of autoclave conditions, there is also an ability to control iron to lower levels such that direct feed to the neutral leach stage is possible but at some expense in the size of the autoclave required.

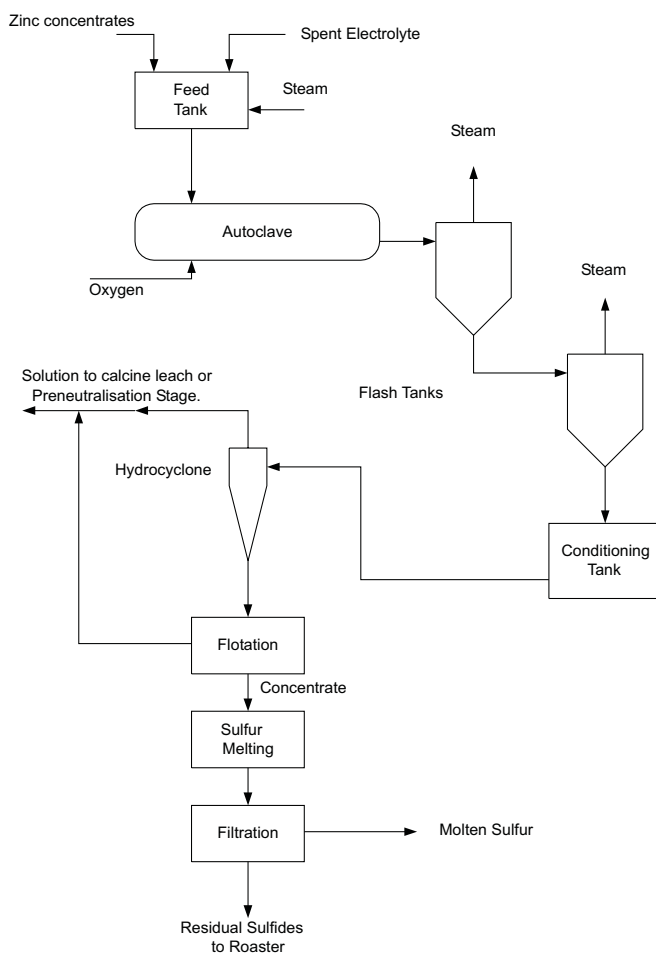


FIG 5.10 - Single stage pressure leach - typical flow sheet.

Hydrocyclone underflow goes to flotation cells, which recover a sulfur concentrate containing elemental sulfur and unreacted sulfides. The concentrate is filtered, dried and melted to enable separation of liquid sulfur from residual sulfides by filtration. The residual sulfide residue can be sent to the roasting plant. Flotation tailings represent a lead-silver residue containing iron and insoluble gangue.

Plant performance depends critically on the nature of the concentrate, its particle size distribution and reactivity. For a single stage operation with a high acid endpoint, the sulfuric acid to zinc in feed molar ratio is controlled in excess of 1.5 and will give final acidities in product solution in the range of 20 to 50 g/L. Zinc extraction can be above 95 per cent for suitably reactive concentrates, and concentrates can require grinding to achieve suitable reactivity. As a guide, regrinding should be to a size smaller than 95 per cent less than 40 microns.

The original Cominco plant had an autoclave of 100 m³ working volume (3.7 m diameter × 15.2 m long) and achieved a treatment rate of over 100 000 t/y of concentrates with an on-line availability of 80 per cent (Ashman and Jankola, 1990).

A list of commercial pressure leaching installations integrated with roast-leach operations is given in Table 5.5.

TABLE 5.5*Commercial single stage pressure leach installations (Buban, Collins and Masters, 2000).*

Plant location (See Table 1.3)	Start-up	Design zinc throughput t/a	Status
Trail	1981	30 000	Closed
Trail	1997	75 000	Operating
Kidd Creek	1983	20 000	Operating
Datteln	1991	50 000	Closed

The conversion of sulfide sulfur in concentrate to elemental sulfur depends to a large degree on the pyrite content (see Equation 5.17), and can range from 60 to 90 per cent.

Molten sulfur processing is handled in the same way as standard technology used in sulfur burning acid plants. The sulfur cake is melted at 140°C with steam and is filtered using a stainless steel filter press with a suitable filter aid precoat. The filtered sulfur can be prilled or solidified into slates.

Marketing of the product sulfur for use in sulfur burning acid plants is difficult due to the impurity content which is primarily mercury and selenium, as well as entrained metal sulfides. Mercury is contained in solid solution in the elemental sulfur as mercuric sulfide. The amount is determined by the solubility in molten sulfur at the conditions prevailing within the autoclave and is in the range of 30 to 50 g/t. If used for sulfuric acid production this would result in a level of ten to 17 ppm in the product acid, which exceeds the normal specification limit of around one ppm. Selenium is strongly bound within the sulfur being chemically similar, and the deportment of selenium in concentrates to product sulfur will be quite high, at two to three times the selenium concentration in the feed concentrates.

Techniques have been developed by Sherritt Inc (now Dynatec) to remove mercury by alkaline leaching but removal of selenium remains impractical. Selenium can affect the conversion catalyst at high levels and will contaminate the product acid (Chalkly, Collins and Ozberk, 1993). Small quantities of entrained metal sulfides can also be present, but can be reduced by double filtration of the sulfur.

In comparison with marketed 'Bright Sulfur' from natural sources or from sour gas, pressure leach sulfur is impure and outlets can only be to specialised acid plants with SO₂ gas cleaning capabilities or where it can be greatly diluted. Consequently, the advantages of pressure leaching over roast-leach, in terms of reduced dependence on sulfuric acid production and disposal, may not be as favourable as might initially appear.

Two Stage Pressure Leaching

For a stand-alone pressure leach based electrolytic zinc plant, a neutral solution is required from the leaching plant prior to solution purification by cementation, and minimum residual acid levels in product solution from the pressure leach are required. For this purpose a two-stage counter-current operation was developed by Sherritt Inc and was installed at the Flin Flon plant of the Hudson Bay Mining and Smelting Company. A flow sheet is shown in Figure 5.11.

In this case, fresh zinc concentrates are fed to an autoclave with solution from the second stage leach together with some spent electrolyte. Zinc extraction is above 75 per cent in the first stage and residual acid is around 8 g/L. Because of the low acidity, most of the iron is precipitated as jarosites and as hydrated ferric oxide, leaving about 2 g/L in product solution.

Residue from the first stage autoclave is leached in the second stage autoclave with spent electrolyte and acidity is maintained above 30 g/L in the exit solution, which goes forward to the first stage.

The first stage product solution is neutralised in two stages with lime to separate a clean gypsum in the first step and to precipitate residual iron in the second, using zinc hydroxide sludges from effluent treatment operations (Krysa, 1995).

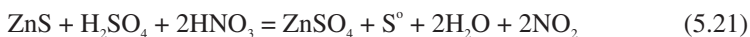
The reactivity of the sphalerite itself varies considerably and can be related to the amount of contained iron as marmatite; the higher this is, the higher is the reactivity. Particle size is also of importance as indicated above for pressure leaching. Reaction rates are however considerably lower than for pressure leaching and residence times of five to ten hours can be necessary. A number of atmospheric pressure direct leaching operations have been installed on a demonstration basis, but few details have been published or made available.

Such processes using iron as the oxygen carrier require removal of iron as goethite prior to purification and electrolysis. But to provide sufficient ferric iron for leaching, recycle of goethite to the leaching stage may be necessary. In this context, it is useful to consider integration of the direct ferric iron leaching operation with the reduction stage of the goethite process (see Figure 5.7).

Low pressure direct leaching systems using iron or the cupric-cuprous couple are much more effective with faster reaction rates if chloride is present or a chloride based system is used rather than a sulfate system. But this requires a considerable departure from established electrolytic technologies and added complications with the generation of chlorine during electrolysis, the use of diaphragm cells and associated construction material requirements. Alternatively, zinc may be transferred from the chloride leach solution to a conventional sulfate system for electrowinning by means of solvent extraction. This is discussed further in sections on Chloride Leaching Systems (Chapter 10) and on Solvent Extraction in Chapter 5.

Nitric acid is also a possible oxygen carrier for use in a sulfate based extraction system as an alternative to ferric iron and gives high reaction rates. However it is necessary to remove nitrates to low levels in solution prior to electrolysis due to the fact that nitrates are reduced at the cathode and will reduce the current efficiency for zinc deposition. Nitrate can be removed by reduction with zinc dust.

The nitrate ion serves as an oxygen carrier for oxidation of the zinc sulfide and can be re-formed both *in situ* and external to the leaching stage. The basic reactions are given in Equations 5.20, 5.21, 5.22 and 5.23.



The oxidation of NO to NO₂ is slow and is the rate determining step. Consequently, it is necessary to externally convert the NO evolved from the leaching operation back to HNO₃ using catalytic oxidation by conventional nitric acid production methods.

A serious complication with this process is the side reaction of NO with ferrous iron produced by the competing reaction of ferric iron oxidation of ZnS. The ferrous iron formed can react with NO to form a highly stable ferrous nitrosyl complex – Fe(NO)SO₄. This can lock-up the active species and cause the leaching reactions to cease. Provided excess nitrate is maintained in the direct leaching stage, the ferric oxidation reaction (Equation 5.14) will not proceed and high leaching rates can be maintained. However failure in control of excess nitrate or excessive addition of concentrate to the leach will cause a drop in redox potential, which in turn will allow the formation of ferrous iron and the immediate cessation of the direct leaching reactions. Because of the stability of the nitrosyl complex this situation is difficult to reverse. This complication has curtailed the development of an otherwise efficient and attractive direct leaching procedure (Bjorling and Kolta, 1965; and Adams, Mangano, Roche and Carpenter, 1990).

Direct Leaching to Sulfate

Oxidation of zinc sulfide is generally aimed at the intermediate stage of elemental sulfur and zinc in solution. Complete oxidation to sulfate according to Equation 5.24 will occur at high temperatures and pressures or under alkaline conditions at atmospheric pressure, such as in an ammonia-ammonium sulfate solution.



Despite the higher reaction rates that are possible under these conditions the outcome is not desirable for a closed system where an outlet for sulfate is required. This is generally provided by neutralisation with lime and precipitation of gypsum. The supply of lime and the disposal of the resulting gypsum adds significant cost to the operations and generally cannot be supported. In this context, one tonne of zinc extracted from a normal concentrate of 52 per cent zinc content would produce around 2.2 t of gypsum.

However, if there is a sulfate balance deficiency in the zinc plant circuit for various reasons, a partial application of full oxidation may give an optimum situation with minimal equipment costs. Some processes have been proposed to use a combination of an initial low temperature pressure leach to extract the bulk of the zinc with production of elemental sulfur, followed by a high temperature pressure leach on first stage leach residue to complete extraction with high efficiency. In particular, the Comproex Process (Nogueira, 1984) uses a low temperature first stage at 140°C followed by a high temperature leach at 200°C to complete the extraction with the formation of sulfate. Excess sulfate is removed from the solution circuit by lime neutralisation to finalise iron removal and other impurities, and to precipitate sulfate as gypsum. The advantages of this system are that iron extracted in the more aggressive second stage can be precipitated as hematite, and jarosites which form in the lower temperature first stage will be decomposed in the second stage, resulting in higher possible lead and silver recoveries from leach residues. The disadvantages are the high gypsum production required but in particular cases this can be optimised to suite the mineralogy of the concentrates processed.

Bacterial Leaching

Bacterial leaching is one form of catalytic oxidation, which utilises certain bacteria such as thiobacillus ferro-oxidans and thiobacillus thio-oxidans to promote oxidation of the sulfides, usually through to sulfate together with solubilisation of associated base metals. Different strains of bacteria are available and usually a mixture of different types provides the optimum approach. Direct sulfide attack by bacteria such as T-ferro-oxidans produce elemental sulfur, which can passivate the mineral surface and prevent further oxidation. It is understood that the oxidation of that sulfur by T-thio-oxidans to sulfuric acid allows the extraction reaction to continue.

Apart from direct attack on the metal sulfides, the bacterial generation of ferric iron in solution and provision of a suitably acid environment, can also allow direct leaching reactions, such as in Equation 5.14, to proceed.

There are also constraints within which the bacteria are viable, such as acidity, metal ion concentrations and temperature although some bacteria (thermophilic) can tolerate temperatures as high as 90°C. It is possible to extend these boundaries with time as increased tolerance to extreme conditions can develop by evolution. Even so, the extraction rate of zinc from a sulfide concentrate is relatively low in comparison with other processes and requires residence times are days rather than hours in duration. Fine grinding is required to improve these rates as indeed it can improve other direct leaching processes.

Another major issue is the low zinc concentrations tolerated by the bacteria, with maxima of the order of 50 g/L. It is not cost effective to consider electrowinning from neutral solutions of this strength and unless tolerance levels can be raised it is necessary to concentrate the zinc content by transfer to a higher strength electrolyte using solvent extraction techniques. The other major concern is the full conversion of sulfides to sulfate requiring elimination as gypsum as detailed above.

Because of these limitations, it is difficult to see competitive application of bacterial leaching processes for 'main stream' zinc extraction processes. There is more opportunity in application to recovery of zinc from tailings or other low-grade materials where heap leaching techniques can be applied to reduce the cost of long residence times, and dilute solutions are indeed necessary to maximise metal recovery.

No significant commercial application of bacterial leaching processes for zinc had been implemented up to the end of the 20th Century. However, continual development of bacterial strains by genetic engineering will no doubt improve performance and broaden tolerance ranges to the point where practical applications can be developed.

Chloride Based Direct Leaching Systems

Many chloride based processes have been defined but without any large scale commercial application to zinc extraction by the end of the 20th Century. Many of these processes were developed for the extraction of a number of base metals from complex ores, which have not been amenable to separation by conventional mineral dressing practices. The value of chloride systems is that all the base metals – copper, zinc, lead as well as silver – can be extracted into solution. A high yield of elemental sulfur is also possible with minimal formation of sulfate. Reaction rates are generally higher for chloride systems than for sulfates, but equipment corrosion problems are severe and for this reason alone many attempted applications have failed on a commercial scale.

The leaching-oxidation medium may be chlorine or HCl/air, which can be recovered and recycled to leaching from the electrowinning operation. Typical processes are the Canmet process (Craig *et al*, 1989), the Cuprex process (Dalton, Diaz, Price and Zunkel, 1991), the Zincex process (Diaz, Martin and Lambers, 1994/5), the Minemet process (Demarthe, Gandon and Georgeaux, 1976) and the Intec process (Everett and Moyes, 1992). Often ferric chloride or cupric chloride are used as the oxidation agent and solvent extraction can be used to transfer zinc from the leaching solution to a separate solution circuit for electrowinning. A compartmented electrolytic cell with a membrane or diaphragm separating the cathode and anode sections is generally needed when using a chloride electrolyte. Chlorine is generated at the anode or alternatively the oxidation agent such as ferric iron can be regenerated by the anode reaction. In that case, depleted catholyte is passed through the anode compartment and the resulting anolyte solution is returned to leaching.

If solvent extraction is used, zinc can be transferred from the chloride leach medium into a sulfate solution for electrowinning using well established and conventional techniques. One example of such a procedure is the CENIM-LNETI process, which uses a low temperature pressure leach in an ammonium chloride solution with oxygen. Zinc is transferred from the leach solution to a conventional sulfate electrolyte by solvent extraction. Iron is separated as goethite in the leach residue and lead and silver are recovered from the leach solution by cementation with zinc dust (Figueiredo, Novais, Limpo Gil and Amer, 1993).

As indicated above, most of these processes have been developed for the treatment of multimetal complex ores and would not compete with conventional single metal extraction processes. Parallel advances in mineral dressing techniques involving finer grinding and fine particle flotation have greatly improved the ability to separate the individual metals from complex ores and have largely obviated the need for multi-metal complex extraction processes. Consequently since the early 1980s when there was considerable interest in these multi-metal extraction process developments, there has been

progressively less justification for large scale commercial development. It would appear that these techniques are probably more relevant in application to smaller scale scavenging operations for the processing of tailings or low grade bulk concentrates, or for the treatment of unusual materials.

SOLVENT EXTRACTION

Conceptually, selective solvent extraction (SX) of zinc from an impure leach solution to a high purity solution for electrowinning, offers considerable simplification of the process flow sheets for the electrolytic zinc process and for the handling of impurities. SX can also allow transfer from one medium for leaching such as chloride, to a different medium for electrolysis such as sulfate, opening the possibilities for enhanced leaching operations while using conventional electrolysis techniques. SX should be able to provide a barrier to a range of harmful impurities from entering the electrowinning circuit.

A conceptual flow sheet for this application of solvent extraction is given in Figure 5.12.

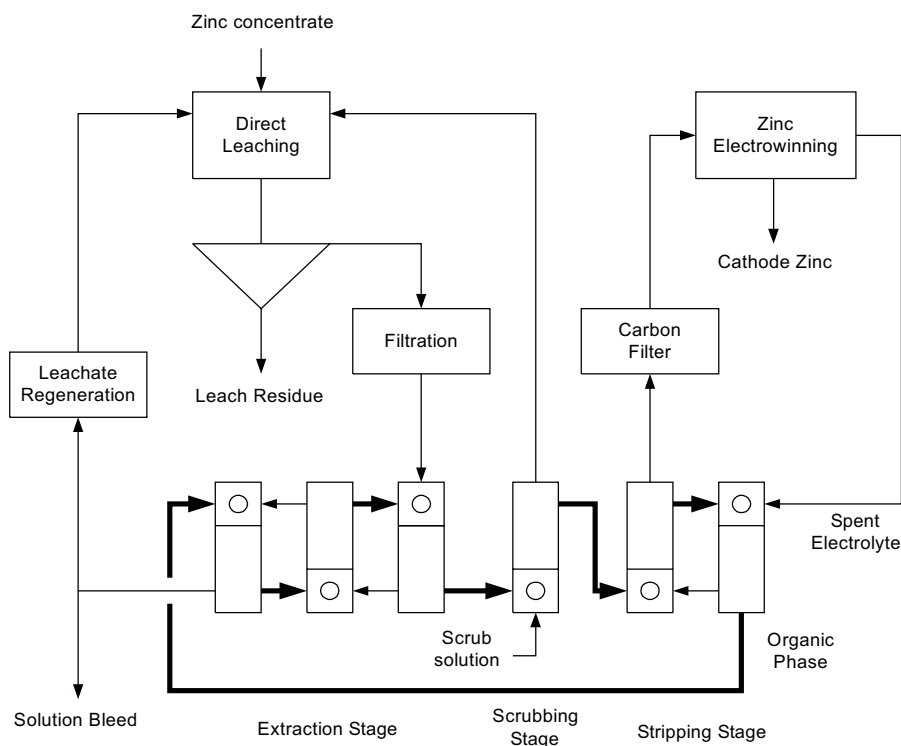


FIG 5.12 - Conceptual flow sheet for the inclusion of solvent extraction.

The initial step is to transfer dissolved zinc from the neutral leach solution (aqueous phase) into the solvent (organic phase) in a series of mixer-settlers representing the extraction step. Generally three or four extraction stages are required.

The organic phase or solvent loaded with zinc is then scrubbed in one stage with a dilute acid solution to remove some impurities, which may have loaded with zinc, and to remove halides, etc. In the final or 'stripping' stage, zinc is recovered from the organic phase by contacting with sulfuric acid as spent electrolyte. The resulting strip solution is recirculated to electrolysis and the barren organic phase is recycled to extraction. There are generally two or three mixer-settler stripping stages required.

This approach assumes that the solvent provides sufficient barrier to minor impurities which are harmful to zinc electrowinning. If this is not the case then a zinc dust purification step will be required before the strip solution is recirculated to electrowinning. This requirement will mean that the strip solution must be close to neutral, which in turn has significant implications to solution flow ratios as detailed below.

Application of solvent extraction in this way will also exclude manganese from the electrolyte, which has implications in relation to the type of anode used. Normal lead anodes used in sulfate circuits require minimum levels of manganese in solution to provide corrosion protection and hence to maintain low levels of lead in the cathode zinc deposit. Manganese would therefore need to be added to the electrolyte from an SX circuit if lead anodes are used, or alternatively DSA titanium anodes may be used in the absence of manganese, but with a high inventory and replacement cost.

There are a number of issues in the application of SX which require careful evaluation for each particular case, and the overall simplicity of the concept tends to vanish when the details are properly examined. This particularly relates to solution flows and corresponding equipment costs.

Solvents

The organic phase used in solvent extraction is made up of an extractant or complexing reagent dissolved in an inert carrier or 'diluent', which is commonly kerosene or comparable commercial equivalents. The diluent can affect the behaviour of the extractant and must be compatible.

An important requirement for the organic phase is the capability of rapid and complete phase separation in the settler after intense mixing, without the formation of an emulsion. The concentration of extractant can influence this by affecting viscosity and often 'modifiers' are added to improve phase separation by increasing surface tension. Long chain alcohols such as isodecanol are often used. The presence of surface active materials can affect the separation and in particular dissolved silica in the aqueous phase can lead to the formation of stable emulsions. It is consequently important to ensure that leach solutions contain soluble silica at levels below 0.5 g/L.

It is found that phase separation is generally better when the aqueous phase is dispersed into the organic phase rather than the reverse. Organic-continuous systems can also tolerate dissolved silica to a greater extent. Optimum results are generally obtained when the organic to aqueous ratio in the mixer-settler is maintained between 1:1 and 2:1. This ratio can be controlled by recycling one stream from the settler discharge back to the mixer.

Unlike the copper industry, the ideal SX system for zinc has been impeded by the absence of a highly selective extractant and also by the possible loading characteristics. The important characteristics of an extractant are:

- selectivity for zinc,
- the solvent loading and extraction recovery achievable,
- impurity deportment, and
- effect of the solvent on zinc electrowinning.

At the time of writing, the most practical extractants or solvents are the alkyl phosphoric reagents as a dimeric species $(RH)_2X.H$ of which di-2-ethyl hexyl phosphoric acid or D2EHPA with a formulation of $[(C_8H_{17}O)_2POO]H$ is the most common example. Each zinc ion extracted reacts with two dimers to form a complex in accordance with Equation 5.25.



The reaction is reversible and driven by the acidity of the aqueous phase.

The important parameter defining the ability of the solvent to extract metal ion M, is the extraction coefficient defined at equilibrium as:

$$E = \frac{\text{Concentration in the Organic Phase}}{\text{Concentration in the Aqueous Phase}}$$

E is dependent on the acidity or pH of the aqueous phase and can be presented as a set of extraction curves for different metal ions. The extraction curves expressed as extraction percentage versus pH for D2EHPA are shown in Figure 5.13.

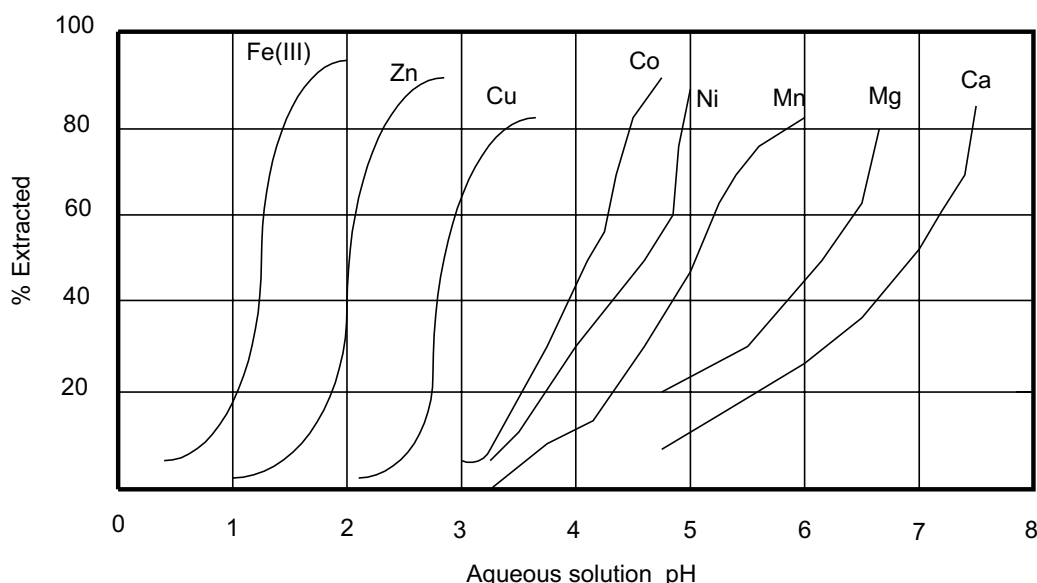


FIG 5.13 - Extraction curves for D2EHPA.

Ferric iron is most strongly held in this case and generally should be removed from solution or be reduced prior to zinc extraction. Careful pH control is necessary to achieve good separation from other metals.

As zinc is extracted acid is generated, altering the position on the extraction curve and the selectivity, and requiring careful pH control and design of a countercurrent multi-stage extraction sequence.

Ferric iron forms a strong complex with D2EHPA and cannot be efficiently removed by stripping with sulfuric acid at the levels encountered in zinc spent electrolyte. Consequently, it must be removed from the solvent using a hydrochloric acid strip. Alternatively, ferrous iron forms a weak complex and can be readily removed. It is possible to reduce the iron complex with the application of zinc dust to the organic solution and hence facilitate the stripping of iron.

The Zincex Process developed by Tecnicas Reunidas SA conducts a dilute sulfuric acid leach to extract zinc and uses D2EHPA to transfer zinc from an impure leach solution to a solution suitable for electrowinning (Díaz, Martín and Lamera, 1994/5).

This process has been commercially applied to the processing of waste dry cell batteries where separation of zinc from manganese and chlorides is the major requirement. There is minimal iron content and hence complications from iron are avoided. The process has been extended to the processing of oxidised zinc ores such as silicates containing high levels of halides, again where the presence of iron is minimal. This procedure is used at the Skorpion Zinc project in Namibia.

Other reagents such as Cyanex 302 based on dialkyl thiophosphinic acid (DEHPT) with a formulation of $[(C_8H_{17})_2POS]H$ have also been developed and applied to zinc extraction but has similar problems with ferric iron to D2EHPA, although it is not as strongly held. Application has largely been for the recovery of zinc from dilute waste streams.

Other attempts have been made to develop highly selective zinc solvents with respect to zinc and iron, notably by Zeneca Specialties as ACORGA DS5869 (Dalton, Tasker and Cupertino, 1995). This reagent showed promise with a high extraction ratio between zinc and iron but had longer term stability problems and did not proceed to commercialisation. It also exhibited strong complexing of copper and cadmium, which were difficult to remove and required hydrochloric acid stripping.

The ACORGA solvent ZNX50 has been developed for chloride systems and is highly selective between zinc and ferric iron. It operates by transferring $ZnCl_2$ rather than Zn^{2+} and is based on a bibenzimidazole molecule. It is only useful for transfer of zinc from chloride leaching solutions to a zinc chloride solution for electrowinning. Selectivity with respect to iron is good but towards copper is relatively low and the level of copper transfer is sufficient to require copper removal from the electrolyte by cementation prior to electrolysis. Similarly DPPP or Diphenyl pentaphosphonate (Bayer) has been developed for chloride systems.

Some development work has focused on the use of solvent extraction for the removal of iron from zinc sulfate leach solutions. Early work evaluated the use of versatic acid for this purpose and considered the extraction of iron using a solvent already loaded with zinc, which is more weakly held than iron and is then exchanged with iron from a secondary leach solution. Zinc is loaded onto the solvent by direct reaction of calcine with the organic phase, but this creates problems with the separation and recovery of solvent from the resulting leach residue (Thosen and Grislingas, 1980).

Versatic acid is a mixture of tertiary monocarboxylic acids. Other work has considered the stripping of versatic acid loaded with iron in an autoclave to form ferric oxide (Collier *et al*, 1986).

The extraction curves for versatic acid are shown in Figure 5.14 and it can be seen that there is a wide separation between zinc and iron with iron being much more strongly held in acidic solutions.

D2EHPA can also be used for iron separation with good effect but, as indicated above, there are difficulties in stripping iron from the solvent.

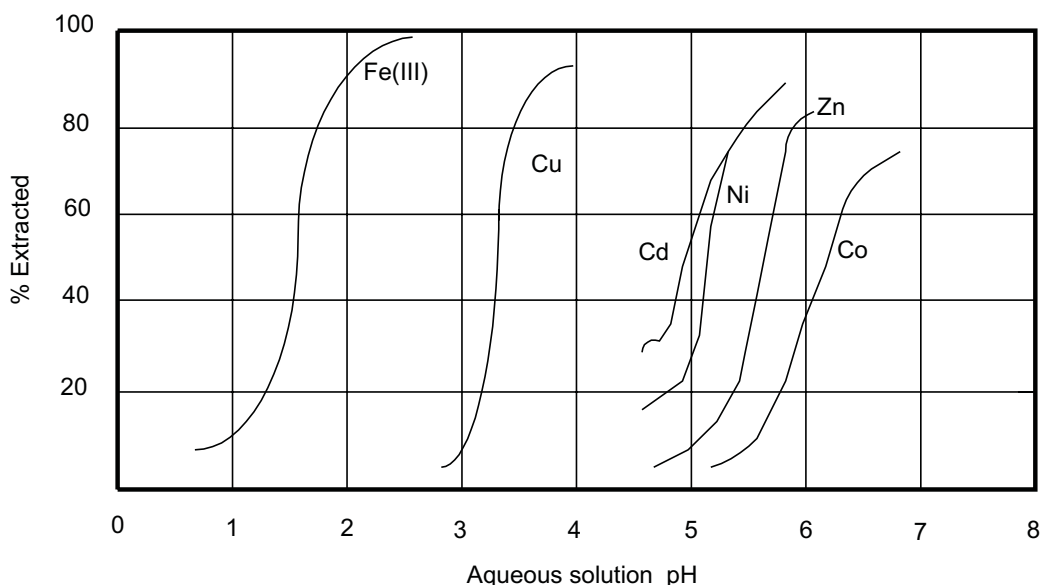


FIG 5.14 - Extraction curves for versatic acid.

Solvent Loading with Zinc

The amount of metal which can be held in the organic phase is the 'loading' and the maximum loading is determined by the molarity of the extractant reagent in the organic phase. Normal practical organic phase solutions are 0.1 to 0.3 molar with respect to the extractant due to its relatively large molecular weight and the need to have low viscosity solutions with efficient phase disengagement. Since two moles of D2HEPA are required to complex one mole of zinc, then for a 0.3 mole solvent solution, the maximum zinc load with full utilisation of the extractant will be 0.15 mole or close to 10 g/L of Zn. This may be raised in higher strength solvent mixes to around 15 g/L Zn at the most.

Low solvent loading is a major issue in the practical application of solvent extraction processes to zinc. For application to normal zinc leach solutions containing around 150 g/L Zn and for electrolytes with concentration differentials between neutral feed solution and spent electrolyte of the order of 100 g/L, exceptionally high organic to aqueous flow ratios will be required. This will mean that organic solution flows will need to be an order of magnitude greater than for normal aqueous solution flows.

As indicated above, for efficient operation of a mixer-settler, an organic-continuous operation is preferred with organic to aqueous flow ratios between 1:1 and 2:1. If overall ratios are outside these limits then it is possible to recycle within each stage. In general with normal zinc plant solution concentrations, a large recycle of the aqueous stream would be necessary or else the flow sheet would need to operate at much reduced and largely impractical zinc concentrations. However, the implications are for greatly expanded solution flows (including recycles) in comparison with normal operations without solvent extraction. This in turn has significant implications for the size of mixer-settler equipment and its cost as well as the cost of solvent inventory and the potential for loss.

In the stripping circuit, it is possible to circulate spent electrolyte through the SX stripping stage and extract only a small amount of zinc per pass. Thus a spent electrolyte at 50 g/L Zn and 150 g/L H_2SO_4 may strip the solvent and report 80 g/L Zn and 105 g/L H_2SO_4 in the return electrolyte. This is practical if, as indicated above, harmful impurities are not transferred and zinc dust purification is not required. If zinc dust purification is necessary then a neutral return electrolyte will be required at a zinc concentration of 150 g/L. In this case, the overall organic to aqueous solution ratio will rise from around 2:1 to 6.7:1.

The consequent costs associated with the handling of dilute solutions are a significant impediment to the application of solvent extraction to normal zinc processing operations. These characteristics essentially mean that solvent extraction is confined to specialised zinc recovery operations from secondary materials or from dilute effluent streams, or from primary sources with unusual impurity contents requiring specialised processing. For these reasons, solvent extraction has not found application to large scale primary zinc production from conventional sulfide raw materials and because of the molecular weight constraints imposed by the nature of the organic extractants, this situation is unlikely to change.

Impact of Organics on Electrolysis

The presence of organics in zinc electrolytes can have serious impact on electrowinning, causing drastic reduction in current efficiency and re-solution of the zinc deposit. Consequently, the application of solvent extraction processes to electrolytic zinc extraction has been viewed with caution and generally avoided where other options are available. If it is to be applied, adequate provisions need to be made to trap and capture any carryover organics contained in feed solution to electrolysis. This can be done by the use of activated carbon filters and by the use of flotation techniques, particularly the use of fine air bubble dispersions to 'float out' and collect any retained organic material. With these measures electrolysis problems can be avoided and zinc can be successfully electrowon from SX strip solutions, as demonstrated by the long term operation of the Zincex Process.

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Solution Purification

PURPOSE

The objectives of solution purification operations are to remove elements that will co-deposit with zinc during electrolysis and hence contaminate the product, as well as to remove elements that reduce the efficiency of zinc electrodeposition by lowering the hydrogen overpotential. The latter effects are discussed in more detail in Chapter 7.

In addition, it is important to remove impurities, which will accumulate in a closed solution circuit. These are elements such as chlorine, fluorine, aluminium, magnesium and manganese. It is also necessary to maintain iron at low levels due to the effect of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple in the electrolytic cell – causing a reduction in current efficiency for zinc deposition by consecutive oxidation of ferrous iron at the anode and reduction of ferric iron at the cathode.

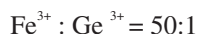
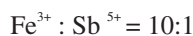
Impurities may be removed by precipitation from solution by means of pH adjustment, or by precipitation as specific compounds apart from hydroxides. In general precipitation by pH adjustment can take place as part of the solution preparation operations, in particular the iron removal stage, with iron being the major impurity to be removed by this means.

Impurities that interfere with zinc electrodeposition can best be removed by displacement from solution (or cementation) with zinc metal. Other highly soluble impurities may need to be removed by a bleed of solution from the closed solution circuit. In particular, this will apply to magnesium chloride and fluoride.

IMPURITY REMOVAL BY PRECIPITATION BY pH ADJUSTMENT

Impurity removal by pH adjustment generally does not require a separate stage and takes place within standard solution preparation operations as detailed in Chapter 5. As discussed in Chapter 5, iron is removed from solution as part of the solution preparation operations in two stages. The bulk of the iron is removed from the system using a number of alternative processes involving the formation of hydrated oxides or basic sulfates. Minor impurity elements such as arsenic, antimony, aluminium, germanium, indium, gallium, and to some extent, copper and thallium can be simultaneously co-precipitated with iron into the iron residue to provide an outlet from the solution circuit.

The neutral leach stage provides an effective step for final separation of these impurities from solution going forward to electrolysis, since it is at this point that the highest pH is encountered (close to five). Iron is lowered to less than 5 mg/L, and significant separation of the above elements also occurs as hydrated oxides or basic salts, generally as homogeneous co-precipitates with iron rather than as separate phases. In this regard the degree of removal can depend on the ratio of the impurity element to iron, and effective removal can only be achieved if the ratio of iron to the particular element exceeds a certain critical level. These ratios depend on precipitation conditions and the presence of other impurities, but may be of the following orders as a rough guide:



Note that As^{3+} and Sb^{3+} are more difficult to remove and require larger quantities of iron.

Impurities separated from solution in this way in the neutral leach stage may be redissolved in the hot acid leach stage and reprecipitated with iron in the main iron removal stage (as jarosite or goethite, etc). Depending on the relative efficiency of the particular iron compound in removing the minor impurity, compared with the neutral leach stage, a circulating load of the particular impurity may

develop, raising the concentration to be handled in the neutral leach. To achieve adequate control of solution going forward to electrolysis in that situation, it may be necessary to add extra iron to the circuit. This is often the case where zinc oxide fume or particularly high grade concentrates are processed.

Elements such as aluminium and silica can also influence the removal of minor elements in the same way as iron. For instance, germanium is particularly co-precipitated with silica, but silica precipitation is complex and the mechanisms, and consequently the separation efficiency, are not fully understood.

The mechanisms for separation of minor impurities with precipitated iron or silica may be co-precipitation but can also be adsorption of the impurity on the surface of the major precipitate. In the case of adsorption the process can be described by the Freundlich Equation 6.1.

$$c = k[V(c_o - c)]^n \quad (6.1)$$

where

- V is the volume of solution per g of adsorbant
- c_o is the initial concentration of impurity
- c is the final equilibrium concentration of impurity
- k and n are constants

As indicated, these removal methods are contiguous with normal leaching and solution preparation operations. Specific solution purification is generally conducted as a cementation operation on neutral leach solution at a pH of 4.8 to 5.4.

IMPURITY REMOVAL BY CEMENTATION (ZINC DUST PURIFICATION)

Principles

The preferred way to remove elements higher on the electrochemical series than zinc is to displace those elements from solution using metallic zinc, since it adds no new components to the solution. This is generally termed 'cementation' and involves the treatment of impure solutions with zinc powder in an agitated tank. The process can be conducted either in a batch or in a continuous flow mode and, for a divalent impurity, proceeds according to Equation 6.2:



The driving force for this reaction is the difference in electrode potentials between the metal (Me) and zinc, and for a divalent metal ion may be expressed by Equation 6.3:

$$E_{\text{Me}} - E_{\text{Zn}} = \{ E_{\text{Me}}^o - E_{\text{Zn}}^o \} + RT/F \ln (\alpha_{\text{Me}} / \alpha_{\text{Zn}}) \quad (6.3)$$

where α is the activity of the metal ion in solution and E_o are the standard electrode potentials for the metals. A list of standard electrode potentials is given in Table 6.1.

In general, the cementation stage is designed to remove copper, cadmium, cobalt and nickel, with cobalt being the most difficult to separate. Most other metals in minor amounts will be adequately removed if efficient separation of the target metals is achieved. There can be particular situations where other impurity elements are unusually high and different targets and controls may be needed, but this is by no means common. Germanium is one example where specialised or modified conditions may be necessary.

The metals with a large difference in standard electrode potential from zinc will have a greater driving force and in general should be cemented rapidly and efficiently – such as copper and lead. Metals closer to zinc such as nickel, cobalt and cadmium will be more difficult to separate. Since the process is electrochemical deposition, many of the principles and controlling factors as discussed in Chapter 7 on Electrolysis will apply. The effects of competing reactions, diffusion resistances and the blocking of the zinc metal surface, and factors such as overpotential for metal deposition will all influence the reaction, and explain why, in practice, the effectiveness of the cementation reaction is much less than would be suggested by Equation 6.3. The zinc surface may be oxidised, particularly if the pH is high, and will thus block the reaction. Precipitated cadmium is more prone to such oxidation than zinc and is more readily dissolved in a neutral zinc sulfate solution from that state in accordance with Equation 6.4:



For these reasons it is desirable to minimise the access to oxygen during cementation operations and in fact blanketing the reaction vessels with nitrogen will assist cementation efficiency as well as providing protection against potential hydrogen hazards. To counteract any tendency for re-oxidation it is also the practice to use excess quantities of zinc dust.

Metal deposition overpotentials are particularly significant. Metallic iron deposition on zinc from ferrous iron solution has a high overpotential and hence the reaction will not proceed. Cobalt and nickel have significant deposition overpotentials on zinc and are more difficult to cement than cadmium. In fact, activators are needed for cobalt cementation.

Copper, cobalt and particularly nickel have low hydrogen overpotentials in comparison with zinc and cadmium. This can result in reduction of hydrogen ions (particularly at low solution pH), and the generation of hydrogen on the deposited metal, coupled with anodic oxidation of adjacent zinc which may dissolve or form a blocking oxide deposit.

The formation of intermetallic compounds by combined cementation can reduce deposition overpotential or provide active sites with lower overpotentials for deposition. Activators work in this way and for this reason arsenic or antimony plus copper may be added as activators for the cementation of cobalt and nickel. The cementation of germanium also appears to require cobalt for activation. Activation of the cementation of a divalent metal ion with arsenic would appear to follow the following reactions:

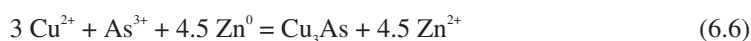


TABLE 6.1

Standard electrode potentials. (Source: CRC Handbook of Chemistry and Physics.)

Electrode Reaction	E° volts
$\text{Ag}^+ / \text{Ag}^0$	+ 0.7996
$\text{Cu}^{2+} / \text{Cu}^0$	+ 0.3402
$\text{As}^{3+} / \text{As}^0$	+ 0.30
$\text{Sb}^{3+} / \text{Sb}^0$	+ 0.10
H^+ / H^0	0
$\text{Pb}^{2+} / \text{Pb}^0$	- 0.1263
$\text{Sn}^{2+} / \text{Sn}^0$	- 0.1364
$\text{Ni}^{2+} / \text{Ni}^0$	- 0.24
$\text{Co}^{2+} / \text{Co}^0$	- 0.28
$\text{Cd}^{2+} / \text{Cd}^0$	- 0.4026
$\text{Fe}^{2+} / \text{Fe}^0$	-0.447
$\text{Zn}^{2+} / \text{Zn}^0$	- 0.7628
$\text{Mn}^{2+} / \text{Mn}^0$	- 1.105
$\text{Al}^{3+} / \text{Al}^0$	-1.662
$\text{Mg}^{2+} / \text{Mg}^0$	-2.375

For cobalt cementation both copper and arsenic are used as activators, and it appears that the reaction given by Equation 6.6 proceeds initially and rapidly, followed by the reactions given in Equation 6.7. The role of antimony is not as clear, although CoSb_2 is known to exist. It probably modifies the zinc surface rather than forming distinct intermetallic compounds with lesser amounts required.

Because of reactions of this type, the performance of any cementation operation can be significantly influenced by the presence and concentration of all other impurities in solution. This can make the removal of some minor impurities particularly complex with variable performance if plant feedstocks are changed.

Solution temperature is an important process variable, particularly if activation is required. This results from the fact that intermetallics such as CoAs and CoAs_2 only appear to be stable above 75 to 80°C. In the case of antimony activation, intermetallics appear to play a less significant role than they do when arsenic is present, and lower temperatures are used than for arsenic activation. Cadmium oxidation and re-solution is enhanced by higher temperature and it is therefore preferred to operate the cadmium removal stage at the lowest possible temperature.

Solution pH is the other process variable which requires careful control. The pH must be low enough to avoid blocking of the zinc surface by basic zinc sulfates, however if the pH is too low there is the danger of direct dissolution of zinc and generation of hydrogen. As indicated above, this can be enhanced by lower hydrogen overvoltages on deposited impurities. The formation of hydrogen can be a hazard due to the risk of explosions, and due to the potential to form the poisonous gases arsine (AsH_3) or stibine (SbH_3) when arsenic or antimony is used as an activator. It is for this reason that arsenic activation is often avoided and antimony preferred since the amounts of antimony used are much lower and the tendency to form stibine is lower under the conditions used. However, it is essential that good ventilation is applied, not only to remove potential exposure of personnel to these hazardous gases, but also to maintain hydrogen concentrations below the explosion limits within the cementation tanks. An alternative is to use nitrogen blanketing, which reduces the ventilation volumes required and essentially eliminates the explosion risk. As indicated above, it will also enhance the efficiency of the cementation reactions to a marginal degree.

Zinc dust sizing and the amount used will clearly influence the cementation reactions by increasing the surface area available for reaction. Zinc dust use represents a circulating load and a reduction in the productive capacity of the cell house. Hence its use needs to be minimised but must be sufficient for the preparation of an adequately purified solution for electrolysis. A fine dust would give the greatest surface area, but is more difficult to produce and handle and oxidises more readily. For some uses, such as for copper and cadmium cementation, a coarse dust is suitable and can be efficiently used, whereas for other cases where cementation is difficult and activation is required, surface area is more important and a fine dust is used. Coarse dust is usually in the range of 100 to 200 microns, whereas fine dust can range from 15 to 40 microns. Zinc dust production is discussed in Chapter 8.

The quantity of zinc dust used is generally expressed as the stoichiometric excess required for the particularly duty. For removal of copper alone, zinc use is relatively efficient and 1.5 to 1.8 times the stoichiometric requirement is generally used. Whereas for cadmium alone the ratio is three to four, and for the cobalt stage may be ten to 12 times. As a performance measure the use of zinc dust as a percentage of cathode zinc is a key indicator and generally ranges from a low of 1.5 per cent up to five per cent or more, but of course depends critically on the mix of impurity elements to be removed, and the zinc dust sizing. Zinc dust use can also be expressed in grams per litre of solution treated rather than percentage of cathode zinc.

Typical pure solution composition ranges achieved following zinc dust purification (or cementation) are shown in Table 6.2.

CEMENTATION (OR ZINC DUST PURIFICATION) PRACTICE

There are a number of different cementation procedures applied depending on the order in which impurities are removed and the conditions and activation methods used. This in turn leads to differences in the system efficiency in terms of overall zinc dust consumption.

With minimal zinc dust addition, copper can always be selectively cemented from solution in an initial stage of any separation procedure. Without an activator, copper and cadmium can be separated with minimal removal of nickel and cobalt. The cobalt and nickel can then be removed by activation in a second stage. Alternatively, if an activator is added to the initial solution with an elevated temperature, copper, cobalt and nickel can be cemented and cadmium can be largely left for removal in a subsequent stage. These broad principles form the basis of most purification procedures.

The two common approaches are the hot arsenic activated first stage, followed by a cadmium precipitation stage, and the cold copper/cadmium removal first stage, followed by a hot activated second stage often using antimony as the activation agent. The first approach was used in the early electrolytic plants and became a normal standard. The second approach developed to improve the recovery of copper and was termed the 'reverse purification' procedure.

Hot Arsenic Activated First Stage Approach

The first stage operates at 85°C with arsenic trioxide addition and zinc dust, and precipitates copper, cobalt and nickel with minor amounts of cadmium. A second stage operates at 70 to 75°C and precipitates cadmium. Often a third polishing stage can be added and the cementate from that stage is recycled to the second stage. Residence times vary from plant to plant but can range from three to five hours for the first stage and one to two hours for the second stage. A generalised flow sheet is given in Figure 6.1.

First stage cementate is leached with spent electrolyte to remove zinc and cadmium, leaving a copper/cobalt residue containing nickel. The leach solution can be passed to the second cementation stage for cadmium recovery. The copper/cobalt residue is heavily contaminated with arsenic, which reduces its marketability and since copper by-product revenue is significant, a more selective copper separation step as a first stage has major advantages. This can be added to remove part of the copper contained in the impure solution, but sufficient must remain in solution to activate the precipitation of cobalt and nickel.

Copper/Cadmium First Stage Approach

In this case, the first stage can operate at low temperature (65°C) to remove copper and cadmium plus lead and some other minor elements such as thallium. Cadmium is recovered by leaching the cementate with dilute sulfuric acid, leaving a copper residue which typically reports around 45 per cent copper, ten per cent zinc, two per cent cadmium and four per cent lead with a significant level of sulfate.

TABLE 6.2

Typical purified solution composition.

Element	Concentration Range	Typical Concentration
Zn	130 - 180 g/L	150 g/L
pH	4.2 - 5.2	4.7
As	0.01 - 0.2 mg/L	0.1 mg/L
Cd	0.1 - 2.5 mg/L	0.7 mg/L
Cu	0.01 - 0.1 mg/L	0.03 mg/L
Co	0.2 - 2.0 mg/L	0.3 mg/L
Fe	0.4 - 10.0 mg/L	7.5 mg/L
Ge	0.01 - 0.1 mg/L	0.02 mg/L
Mn	2.5 - 15.0 g/L	5.0 g/L
Ni	0.05 - 0.5 mg/L	0.1 mg/L
Sb	0.01 - 0.2 mg/L	0.01 mg/L
Tl		0.1 mg/L
Cl	50 - 1000 mg/L	250 mg/L
F	1 - 200 mg/L	15 mg/L

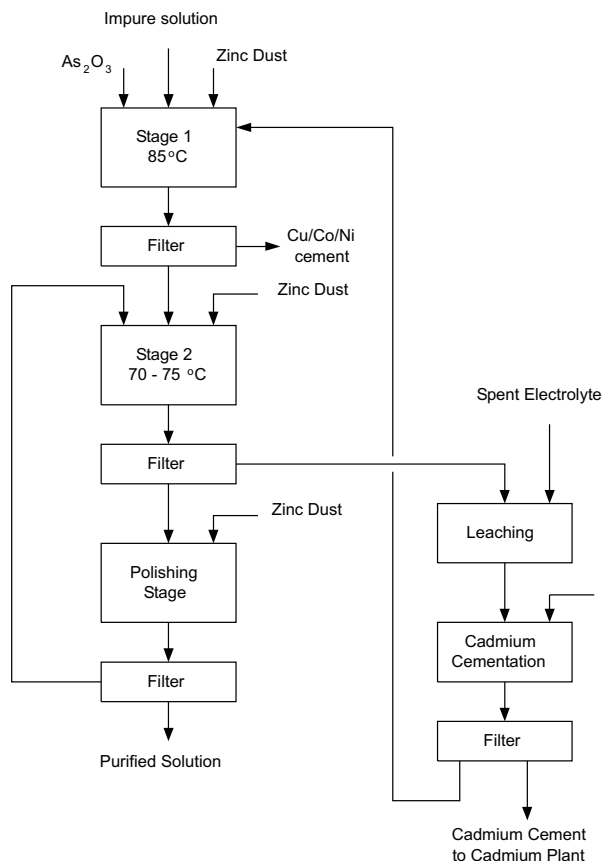


FIG 6.1 - Generalised flow sheet – hot activated first stage purification.

The second cementation stage is hot, at around 80°C, and uses arsenic or antimony with copper sulfate additions for activation. This gives a copper/cobalt/nickel cementate. A generalised flow sheet is given in Figure 6.2.

Union Minière have developed a variant of this approach in which the first stage is operated in two steps, with coarse zinc dust addition to the first tank to precipitate predominantly copper, followed by further zinc dust additions in subsequent tanks to complete the precipitation of cadmium. The cementate recovered from this procedure contains a greater separation of copper and cadmium particles and consequently makes the leaching of zinc and cadmium from the cementate easier, thus raising the grade of the copper residue.

The cobalt/nickel stage operates at a relatively low temperature of 70°C but with a particularly fine zinc dust (D50 = 16 microns) and with the addition of copper sulfate and antimony trioxide (Bellefroid, 1985).

Selective Copper Removal First Stage

This may be regarded as a variant of the hot arsenic activated first stage approach and an efficient variant has been developed by Outokumpu at the Kokkola smelter. The first stage uses a coarse zinc dust with a residence time of around one hour and aims to precipitate copper (and lead), leaving up to 80 mg/L of copper in solution for subsequent activation of cobalt removal. Copper residues containing over 70 per cent copper can be produced and significantly improve by-product returns.

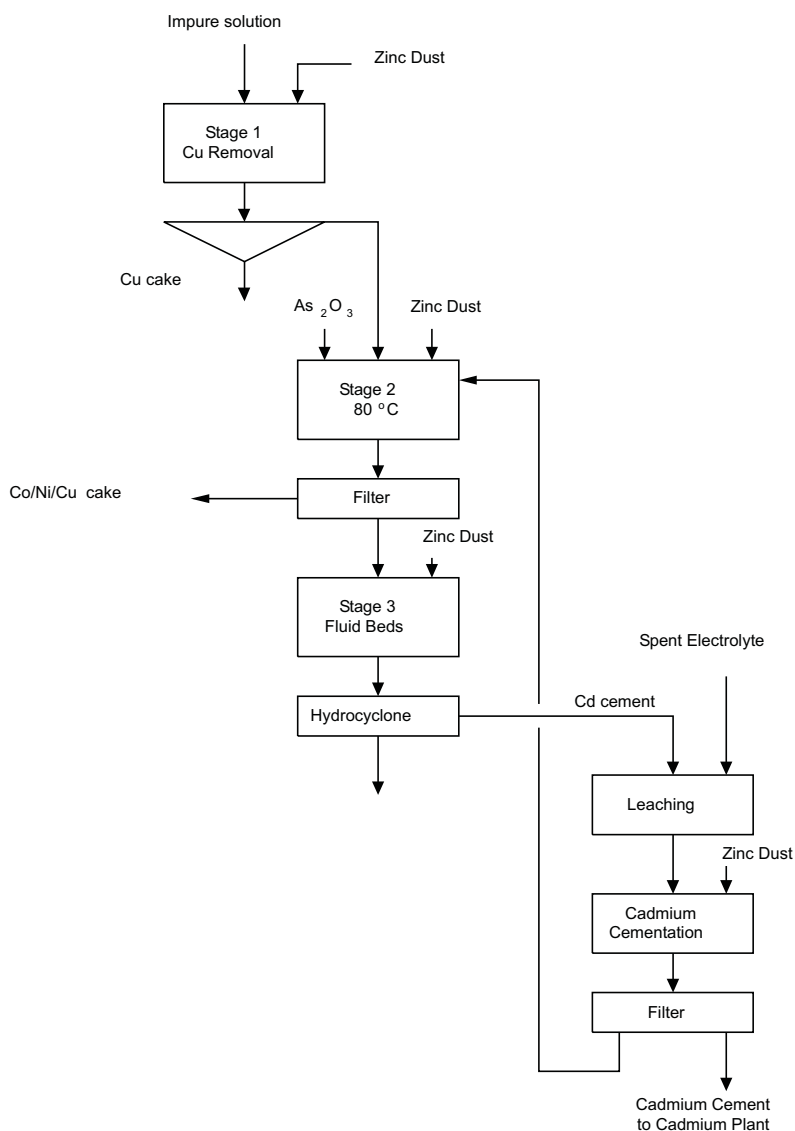


FIG 6.3 - Generalised Outokumpu purification process.

The disadvantage is the heavy contamination of the cobalt residue with cadmium. The use of arsenic activation would not allow cadmium to co-precipitate with cobalt and nickel, and a separate cadmium removal stage would be necessary (Pammenter, Gilmour and Salmon, 1993).

There are indeed many variations of these generalised flow sheets, but all follow the broad principles outlined above.

EQUIPMENT USED FOR CEMENTATION

Cementation is conducted in a series of agitated tanks into which zinc dust is added at a metered rate either in dry form or as a slurry in water. Each stage is generally followed by a filter to separate the cementate.

The type of filter used is a critical feature of the solution purification plant and requires careful evaluation. As noted earlier in this chapter, the precipitate can be prone to oxidation and re-solution, which is particularly the case for cadmium. This can occur during filtration and tends to increase as the precipitate ages. It is therefore common practice to monitor filtrate continuously and discontinue filtration and discharge the filter cake when the cadmium level in the filtrate starts to increase. It is clearly critical to discharge the filter cake quickly and cleanly without leaving residual material to contaminate the following cycle. Clean filtration without any solids leakage is also a key feature, since solids leakage is often the cause of poor purification performance.

Batch-operated recessed plate and frame filter presses or pressure leaf filters are normally used for these operations. Various automated units are available, but it is important that efficient cloth cleaning is employed and used between each cycle. Cloth attachment needs to be sound to avoid leakage of solids and to avoid the potential of cloth damage during discharge operations. Pressure leaf filters with rotating disc elements have proved troublesome in this regard. Fixed leaf filters are generally more robust. Some pressure leaf filters discharge cake by sluicing with impure solution, but can lead to process and flow sheet complexities due to the low slurry density of the discharged cake which may require secondary filtration before further processing.

With batch-operated filters it is also necessary to recycle solution at the commencement of a filtration cycle to capture any solids leakage or out of specification solution in the initial flush. This allowance must be built into the design capacity of the filtration system. It also emphasises why continuous on-line analysis of purified solution is an important feature.

Where coarse zinc dust is used with rapid cementation reactions, such as for copper, when oxidation and re-solution is not an issue, a settler can be used to separate the cementate in place of a filter. Similarly in the case of the Outokumpu fluid bed system for cadmium cementation, no filters are necessary and a hydrocyclone is normally used for separation of final solids.

A large clarifying tank is often used for final clarification of purified solution to capture any residual solids before addition to the electrolysis circuit. With operation at a pH of five and cooling of the solution, basic zinc sulfate can precipitate in minor amounts in this tank and aids the capture and separation of residual solids from the cementation operation. The settler-clarifier is not equipped with rakes and is cleaned of captured solids only spasmodically. Design of these tanks is usually in the form of a large surface area with a narrow conical base and are referred to as 'champagne glass settlers'. In normal operation, the benefits of these tanks are marginal. In a similar way, large storage tanks for purified solution also serve to settle out residual solids. Care must be taken not to pick up any settled solids into electrolysis feed solution as these can deliver a concentrated slug of impurities to the cell house and cause major disruption to the electrodeposition of zinc. Tank cleaning must ensure that the tanks are isolated and all sludges are carefully removed into the leaching circuit.

Analytical Control

Analysis of purified solution is a critical feature of the solution purification operation, to ensure the quality of solution delivered to electrolysis and also for the purpose of control of zinc dust additions. Continuous on-stream analysis is now common, although in the past a full shift laboratory service was often provided. Elements monitored are cadmium, lead, antimony, copper, cobalt and nickel. Voltammetric methods are the common choice for the low levels encountered, although colorimetric methods are also used for cobalt.

It is important to acidify samples before analysis to ensure that any residual cementate in suspension is dissolved.

Another important feature of the purification plant is the ability to divert and recycle solution that does not meet pure solution quality specifications. It is also common to use statistical process control charts for the presentation of analytical data on pure solution quality.

OTHER SOLUTION PURIFICATION METHODS

Cobalt and Nickel Separation as Organic Complexes

The practice of separation of cobalt and nickel as organic complexes was used more extensively in the past. A better understanding of zinc dust cementation has improved that operation and largely supplanted the use of organic reagents. Not only are the organic reagents expensive but there are dangers with excess reagent affecting the electrolysis operation.

Cobalt can be precipitated highly selectively as a complex of alpha-nitroso-beta naphthol. The reagent is prepared by mixing 100 parts by weight of beta naphthol with 48 parts of sodium nitrite and 30 parts of sodium hydroxide. This produces $\text{OH} - \text{C}_{10}\text{H}_6 - \text{NO}$, which strongly complexes cobalt. Iron will also be complexed and must be less than 2 mg/L in the solution treated. The impure zinc sulfate solution containing cobalt is treated with the resulting reagent at pH two to three for up to two hours residence time to precipitate all the cobalt. It is important that excess organic reagent does not carry through with the purified solution and either a limiting lower level of cobalt is retained in solution to ensure that all reagent is consumed (around 5 mg/L), or else an excess reagent removal procedure using activated carbon must be used (Miyaji, Sakata and Suzuki, 1984). The resulting cobalt complex is filtered from solution and may be burned in a furnace to yield a cobalt oxide (Co_3O_4). This will tend to be contaminated with iron and some retained zinc, but is a marketable by-product.

Nickel may be removed from purified solution following cobalt separation as above using dimethyl glyoxime. Generally, this will be heavily contaminated and further processing for nickel recovery is unlikely to be justified.

Chlorine Removal

Generally, the roasting of zinc concentrates achieves over 90 per cent separation of chloride from zinc calcine and controls the level of input to the solution circuit. This is normally sufficient to maintain a balance with losses in residues, etc, which results in an equilibrium concentration of chloride in circuit solution within acceptable levels.

However chlorine may effectively be removed as cuprous chloride within a separate primary copper cementation stage, provided less than stoichiometric zinc dust is used and residual copper is left in solution – as is the case with the Outokumpu procedure above. Around 5 to 10 mg/L of chlorine can be removed per pass in this way, which is equivalent to 0.005 per cent to 0.01 per cent of the zinc throughput. This can provide an effective control measure in all but extreme cases of high chlorine intake levels.

Another direct chloride precipitation method involves the use of silver chloride. In this method silver sulfate is added to the purified zinc sulfate solution to precipitate silver chloride, which is filtered from the solution. A residual level of chloride is maintained to avoid the use of excess silver sulfate and consequent loss of silver. The resulting silver chloride precipitate is treated with dilute sulfuric acid and zinc dust to form metallic silver and a zinc chloride solution. The metallic silver is mixed with concentrated sulfuric acid and heated in a furnace to reform silver sulfate and fume off any excess acid. The resulting sulfate is ground in a ball mill ready for re-use. Notwithstanding that excess reagent use is avoided, there are significant losses of silver to solution and this method does involve a significant cost.

Thallium Removal

Thallium is normally effectively removed from the zinc circuit during cementation and tends to report with cadmium. It will concentrate in the cadmium recovery plant and can be returned to the zinc circuit in any solutions returned for the purpose of zinc recovery and control of the concentration of zinc in the cadmium plant solution. In that event, a circulating load can be established leading to high levels of thallium in zinc electrolyte. Thallium will not affect current efficiency but will contaminate the cathode

deposit and tends also to increase the level of lead in cathode zinc. Thallium normally co-precipitates with iron in iron residues, and for this reason return solutions from the cadmium plant should enter the zinc circuit ahead of an iron separation stage. If the level of thallium in feed materials is high then build-up is possible and an additional outlet has to be provided. This outlet is best located where the concentration is the greatest, which is in the cadmium plant.

The method used for thallium precipitation involves treatment of a neutralised solution with potassium permanganate to precipitate thallium. Sodium bichromate may also be used.

Germanium Removal

Generally, germanium can be adequately controlled by co-precipitation with iron into iron residue and by zinc dust cementation, even in extreme cases. There are indications that the presence of cobalt is necessary to activate the cementation of germanium and long residence times are required.

A number of specific solvent extraction techniques have been developed for germanium separation from zinc sulfate solution, such as LIX63 (deSchepper, 1976) and Kelex 100 (Cote and Bauer, 1980). Often these are only applied to a specialised solution from the leaching of feeds in which the concentration of germanium is particularly high. Such a case may be the leaching of zinc oxide fumes, and will represent a secondary stream in a large electrolytic zinc plant.

Germanium may also be precipitated by tannic acid as germanium tannate, which can be separated and treated to recovery germanium. This procedure is not selective and arsenic and antimony in particular are co-precipitated. The reagent is also relatively expensive.

REMOVAL OF GYPSUM

The normal presence of calcium in concentrates as limestone or dolomite gangue minerals is sufficiently high to ensure that solutions are always fully saturated with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The solubility of gypsum in zinc sulfate solution rises with temperature to a peak at around 50 to 60°C and then declines. Together with its ability to readily form supersaturated solutions, this behaviour leads to serious scaling problems on both cold surfaces such as piping and hot surface such as heat exchangers. Scaling in solution pipe lines and in electrolyte cooling towers can be particularly severe and extensive regular cleaning of gypsum deposits is normal practice. The cleaning load can be high in the cell house and be a significant cause of loss of plant availability. This particularly applies to the electrolyte cooling towers and for these reasons the inclusion of a gypsum removal stage on purified solution can be cost effective.

Gypsum removal is achieved by cooling purified solution from a temperature of around 70°C to 20°C in a series of unpacked evaporative cooling towers. Fine gypsum is added to the solution prior to cooling to serve as seed. Solution pH is held at five or below to prevent the formation of basic zinc sulfate and loss of zinc in the resulting gypsum. Cooled solution flows from the towers to a thickener and clarified solution passes on to electrolysis. Thickener underflow is screened using a sieve bend or DSM screen. The fines are recycled as seed and the coarse fraction goes to a belt filter with washing facility. Washed coarse gypsum can be sufficiently free of contamination for disposal as a by-product.

This installation has a dramatic impact on the cleaning requirements in the cell house as well as throughout the rest of the plant. This will generally also improve plant availability and hence throughput.

RECOVERY OF BY-PRODUCT METALS

Copper

As detailed above, copper cementates may be separated as part of zinc dust purification in various qualities or grades, depending on the flow sheet used. The best grade material is recovered from a separate primary cementation stage, in which above 70 per cent copper grades can be achieved.

Otherwise the copper residue can be heavily contaminated with arsenic or, to a lesser degree, with antimony, depending on the method of activation used.

The copper cementate is normally sold to copper smelters who apply penalties for impurity elements, particularly arsenic and cadmium.

Cadmium

Integrated with all the various cementation processes are various means of recovering cadmium metal as a by-product. Most methods rely on the leaching of the relevant cementate with spent zinc plant electrolyte to extract excess zinc dust and cadmium. Cadmium is separated from the resulting solution by further cementation with a minimal excess of zinc dust, is filtered and the filtrate returned to the zinc circuit to join the impure solution stream ahead of zinc dust purification.

The high grade cadmium cementate from the above procedure may be re-leached in dilute sulfuric acid (cadmium spent electrolyte) to provide feed solution for electrowinning cadmium or it may be briquetted and melted under caustic soda to produce a crude 'caustic' cadmium metal, which can be further refined by vacuum distillation. Vacuum distillation can be relatively simple and compact, and can use mild steel equipment if the level of zinc in the primary feed material is reasonably low. The boiling point of cadmium is 765°C compared with 907°C for zinc, hence a good separation is possible by distillation. The relative vapour pressures of zinc and cadmium at different temperatures are given in Table 6.3.

TABLE 6.3
Vapour pressures of cadmium and zinc.

Temperature °C	767	650	500
Cd vapour pressure (mm Hg)	760	184	15
Zn vapour pressure (mm Hg)	156	29	2
Ratio of vapour pressures Zn:Cd	0.205	0.158	0.133

Clearly the separation will be enhanced under reduced pressure. The required duty of the equipment will be reduced, enabling the use of mild steel equipment and containment to reduce health and environmental hazards.

Alternatively, the cadmium-rich solution derived from zinc plant cementate leaching can be purified by selective cementation with zinc to remove any traces of copper, by treatment with di-methyl glyoxime to precipitate traces of nickel, by treatment with permanganate to precipitate thallium as outlined earlier in this chapter, and by treatment with sodium carbonate to separate any traces of lead. Cadmium can then be cemented from the resulting purified solution with a minimal of excess zinc dust and the cadmium cement briquetted and melted under caustic soda to produce a 'caustic cadmium' suitable for direct sale as high grade cadmium metal (99.99 per cent). The caustic soda flux used in the melt refining processes extracts any residual zinc and can be returned to the zinc circuit at an appropriate point, such as the iron precipitation stage.

Electrowinning of cadmium is similar to zinc using aluminium cathodes and lead anodes. There is a strong tendency to form dendritic deposits, and to avoid this low current densities must be used, generally between 60 and 100 amps/m², with deposition times of the order of 48 hours. Electrolytic feed solution may be 100 to 200 g/L Cd and 40 to 100 g/L Zn, and the acid concentration of spent electrolyte is in the range of 100 to 180 g/L.

Cadmium cathodes are usually stripped manually and melted under caustic soda. Molten cadmium is generally cast into either rods or ball shapes. Generalised flow sheets of the cadmium options are illustrated in Figure 6.4.

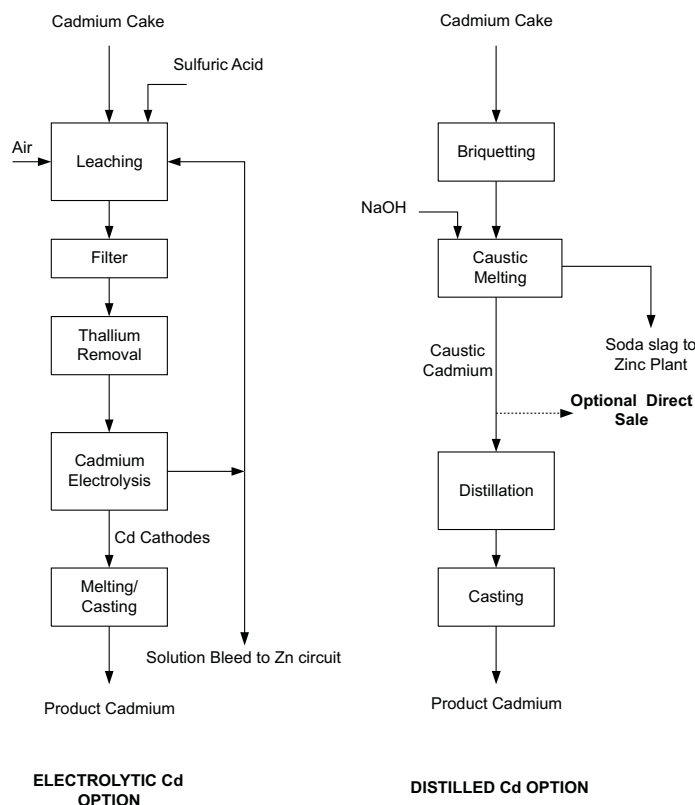


FIG 6.4 - Generalised cadmium production options.

Particular concerns with cadmium operations relate to hygiene and environmental emissions, particularly from melting and casting operations. Extensive ventilation and fume collection is required to meet cadmium-in-air limits. Mist from the electrolytic cells can also be a source of cadmium in air and requires particular attention.

SUMMARY OF THE BEHAVIOUR OF IMPURITIES, THE EFFECT ON ZINC ELECTROWINNING AND CONTROL METHODS

The control of minor impurities is the critical feature of the electrolytic zinc process and rigorous solution purification procedures are required. Many of the details have been discussed under Solution Preparation in Chapter 5, Solution Purification in Chapter 6, and Electrolysis in Chapter 7. The following provides a summary of the impact and control of the range of impurities normally encountered. The impact of the impurity on current efficiency is given below in some instances. This is an order of magnitude guide only, since combined effects with other elements can be significantly different from individual effects and this must always be considered in any process evaluation.

Aluminium

Aluminium dissolved from calcine is precipitated with iron in the iron removal stage at a pH of around four as aluminium hydroxide. However, depending on the efficiency of precipitation and the inclusion of an acid wash of the iron precipitate, aluminium levels can build up in circuit solution. The concern is then the increase in ionic strength of the solution and the reduction in sulfate available for zinc.

Increases in solution density and viscosity will also impact on settling and filtration performance and to some extent will impact on electrolytic cell voltage. There are no effects on electrode reactions during electrolysis. Aluminium can form complexes with fluorine and reduce the impact of that element in causing sticking of the zinc deposit to the cathode.

Antimony

Antimony is particularly harmful in reducing current efficiency and the impact may be around a 35 per cent reduction in current efficiency at 1 mg/L. The impact is greater in the presence of cobalt and germanium.

Antimony is usually controlled to less than 0.02 mg/L. It can be present in the trivalent or pentavalent form. The trivalent form is efficiently removed by iron during iron precipitation but the pentavalent state is more difficult to control and can be a source of current efficiency problems.

Antimony can be added to electrolysis in the form of potassium antimonial tartrate together with agents such as animal glue for the purpose of leveling the zinc deposit. In this application, it probably acts by enhancing the re-resolution of surface projections.

Antimony addition rates may be of the order of 1 g per tonne of zinc deposited, which represents approximately 0.1 mg/L. The corresponding quantity of glue added is much greater and is necessary to neutralise any adverse impact of the added antimony on current efficiency.

Arsenic

Arsenic has substantially less impact on current efficiency than antimony in the ratio of about 5:1, and levels of the order of 0.1 mg/L in purified solution can be tolerated. It is efficiently removed by co-precipitation with iron. As for antimony it can be present in solution in both trivalent and pentavalent states, with trivalent arsenic being the most readily removed.

Barium

Barium sulfate is highly insoluble and generally reports to the leach residue, with no impact on the electrolytic process.

Bismuth

Bismuth compounds are also highly insoluble in the sulfate solutions. Bismuth reports to the leach residue, generally following lead.

Cadmium

Cadmium will not affect the electrolysis of zinc solutions but will co-deposit preferentially and contaminate the product zinc. The Special High Grade (SHG) specification for cadmium in zinc is less than 0.003 per cent, which requires the concentration of cadmium in pure solution to be less than 3 mg/L. To avoid the impact of extreme variations, target levels are generally up to an order of magnitude lower at less than 0.3 mg/L. This is also an indicator of good purification performance.

Calcium

Calcium has no effect on electrochemical processes. However gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has relatively low solubility and a peak solubility between 50 and 60°C, resulting in supersaturation of plant solution due to temperature changes and deposition of gypsum scale on both hot and cold surfaces. Resulting cleaning requirements are a significant operating load and a cause of equipment downtime. For this

reason, a gypsum removal stage is often included in the plant circuit following purification and prior to electrolysis. Pure solution is cooled to around 20°C in the presence of fine gypsum seed, allowing gypsum to be crystallised from solution and separated. Reheated solution will be unsaturated and give far less scaling problems. Levels of calcium in solution range between 300 and 800 mg/L.

Chlorine

Chloride can be oxidised at the anode to form chlorine gas if the concentration is above 300 mg/L. This is a principal cause of anode corrosion, and for this reason it is generally controlled below 200 mg/L. Alternatively, perchlorate can be formed and the relative amount depends on the anode oxidation potential, which can be modified by the concentration of manganese in solution. New anodes favour the generation of chlorine as do pure lead anodes in comparison with anodes alloyed with silver. The evolution of chlorine gas can also be a health hazard and is usually experienced with the initial use and 'running-in' of new anodes (see Chapter 7).

Anode corrosion results in the transfer of lead to the cathode deposit and is the primary contaminant of cathode zinc. Hence these issues relating to chloride levels and electrode potential control are important.

Primary control of chlorine input is by volatilisation during roasting, which eliminates over 90 per cent of the chlorine contained in concentrates. Direct leaching of concentrates clearly can be associated with significant chlorine control problems. Otherwise, separation from the plant circuit can be by solution bleed, or by direct removal with the precipitation of cuprous chloride or silver chloride.

Cobalt

The presence of cobalt will reduce current efficiency for zinc deposition, with an indicative loss of 15 per cent for an increment of 10 mg/L. In excess, cobalt causes pinholing of the zinc deposit. Cobalt can reduce anode voltage and hence anode corrosion, and from this viewpoint can also be beneficial. Plants operating with high cobalt levels in solution can use pure lead anodes with no silver content. The effect of cobalt is complex and depends on the presence of other impurities, particularly germanium. Some plants have operated with cobalt levels up to 8 mg/L in purified solution, but require an efficient iron precipitation stage and low levels of residual iron in solution, which may in fact be indicative of the efficient removal of a range of other associated impurities. However, it is generally desirable to operate with low levels of cobalt at around 0.2 mg/L.

Cobalt is the most difficult of the usual impurities to remove by zinc dust cementation and usually dictates the processing parameters for that operation. If cobalt levels are below 0.2 mg/L, then it usually indicates that other deleterious impurities will also be efficiently removed. Other forms of cobalt removal such as the use of organics are discussed earlier in this chapter.

Copper

Copper will also preferentially deposit during zinc electrodeposition and has the effect of lowering hydrogen overvoltage thus reducing current efficiency. The impact can be around five per cent loss of current efficiency at 1 mg/L. However, copper is readily removed by zinc dust cementation to low levels, generally around 0.03 mg/L. The principal source of copper in the electrolyte is probably from the corrosion of electrode contacts and headbars, as well as power supply bus bars. This is an issue for careful monitoring and for good housekeeping practices in the cell house.

Fluorine

Fluorine in excess of 20 mg/L in an electrolyte will cause sticking of the zinc deposit to the aluminium cathode sheet and will interfere with the stripping operation. In the extreme, the deposit cannot be removed and the zinc must be dissolved by pickling the cathode sheet in spent electrolyte. Fluorine can form complexes in solution such as with aluminium, which will reduce its effect on the cathode.

As for chlorine, primary control is generally by volatilisation during roasting and similar levels are eliminated. Otherwise, fluorine is precipitated with iron in the iron removal stage and the amount removed is proportional to the quantity of any hydrated iron oxide precipitated. No fluorine is precipitated by pure jarosite. Goethite or paragoethite appear to be far more effective for fluorine rejection. The bleed of circuit solution is another effective means of control.

Gallium and Indium

Generally, these elements are not a concern and are effectively precipitated with iron. If present in significant amounts, they can be recovered as by-products. In such a case they are precipitated by neutralisation of acid leach solutions. The Iijima zinc plant in Japan uses calcium carbonate to neutralise a leach solution in which the iron has been reduced to the ferrous state. The gypsum produced at high pH is enriched with indium and gallium, and is treated for recovery of these elements (Yamada, Kuramochi and Togashi, 2000).

Germanium

Germanium has a large impact on current efficiency for zinc electrodeposition with a loss in excess of 50 per cent for 1 mg/L in solution. Removal from solution is achieved by co-precipitation with iron and by zinc dust cementation, although it has been found that removal by cementation does require the presence of cobalt for activation. When significant amounts are present in zinc concentrate feed (ie above 15 g/t), both methods are needed to obtain sufficient protection of the zinc electrolysis operation.

As discussed earlier in this chapter, other methods of germanium separation include solvent extraction and precipitation with tannic acid. If present in large amounts, an iron residue can be produced containing up to one per cent Ge, which can be used for subsequent recovery.

Iron

The action of iron in the electrolyte is to be consecutively oxidised to ferric iron at the anode and then reduced to ferrous iron at the cathode. This provides an alternative set of electrode reactions reducing the current available for zinc deposition and hence reducing current efficiency for zinc electrodeposition. The loss of current efficiency may be of the order of three per cent at 10 mg/L. Otherwise there are no harmful effects on the process.

Because iron precipitation is a means of removal and control of many other minor harmful impurities, low levels of iron in solution can be an indication that adequate removal of these impurities has been achieved.

Lead

Lead is primarily a contaminant of the zinc deposit and is derived from the anode. It will raise the hydrogen overpotential and hence can improve current efficiency. The Special High Grade (SHG) specification for zinc requires less than 0.003 per cent lead, which requires less than 3 mg/L in solution.

Apart from the fact that lead sulfate has low solubility, lead is normally efficiently removed by zinc dust cementation and is minimal in purified solution. The source of the lead is primarily the anode and control is firstly achieved by minimising anode corrosion (see chlorine above). The presence of manganese in solution and formation of a manganese dioxide coating on the anode are critical in maintaining low levels of lead in the zinc deposit, as is the use of lead anodes alloyed with silver at around 0.5 per cent. In addition, strontium carbonate is often added to the electrolyte as a regular dosing to control lead. Strontium sulfate is precipitated and co-precipitates lead sulfate or adsorbs lead to maintain suitably low levels of lead in solution close to the cathode.

Often the use of strontium is excessive, as it is seen as a panacea for lead problems, but at significant cost. Control should be at a level of around 25 mg/L of strontium addition to the electrolyte and addition should be closely controlled and continuous rather than shock dosing when a problem arises.

Magnesium

Magnesium has no impact on the electrode processes but its accumulation raises the density and viscosity of the electrolyte. It raises solution molarity for a given zinc concentration, and will limit the maximum potential concentration of zinc in the electrolyte.

Density and viscosity effects impact on the conductivity of the electrolyte and raises the cell voltage. Cell voltage may be raised by around 0.12 per cent per 1 g/L Mg. In addition, settling and filtration operations are adversely affected limiting throughput, and the presence of magnesium will reduce the capacity of the solution to hold zinc. For these reasons it is desirable to limit magnesium concentrations to less than 10 g/L. Control is possible by a solution bleed and by an acid leach of concentrates prior to roasting. High levels of magnesium in concentrates usually attract a penalty in the purchase terms.

Manganese

Manganese is beneficial and its presence is essential with the use of lead anodes by forming a protective manganese dioxide coating. It has no impact on the cathode process but as for magnesium it will reduce the capacity of the solution to hold zinc and will raise the density and viscosity of the electrolyte, increasing cell voltage. Cell voltage may increase by 0.05 per cent per 1 g/L Mn.

Manganous ions are oxidised at the anode to form MnO_2 . The actual mechanism for MnO_2 formation is partly the formation of permanganate at the anode surface, which reacts with manganous ions in solution to form MnO_2 , some of which adheres to the anode and the remainder falls to the bottom of the cells as anode sludge. The proportion adhering is influenced by the concentration of manganese, the cell temperature, current density, acidity of the electrolyte, the presence of cobalt and iron, and by the age of the anodes. New anodes will cause a higher precipitation rate. The presence of permanganate ions gives the spent electrolyte its characteristic pink coloration.

Precipitation of MnO_2 provides a means of control of manganese in solution and usually it is necessary to recycle MnO_2 through the leaching stage to maintain the desired levels in solution at a minimum of 3 to 4 g/L. The principal concern for high levels is the frequency of cleaning of both anodes and cells and, if in excess, the cleaning requirements can severely disrupt cell house operations. For these reasons solution concentrations will be maintained at minimum levels to ensure adequate anode protection. This is normally in the range of 4 to 7 g/L Mn, but up to 12 to 15 g/L is tolerable. This may normally correspond with a level of Mn in concentrates of around 0.5 per cent. Solution bleed is another means of control of additional manganese inputs.

Mercury

Mercury can raise the hydrogen overvoltage and improve current efficiency by around two per cent for each 10 mg/L. However mercuric sulfate is insoluble and mercury will generally report to the leach residue. Zinc dust cementation will also control mercury in solution to very low levels and its presence is not an issue.

Apart from the above solution controls, mercury is primarily removed by volatilisation during roasting. Separation from gases proceeding to sulfuric acid production is necessary to control the levels of mercury in product acid (see Chapter 4).

Nickel

Nickel reduces current efficiency and causes re-solution and pinholing of the zinc deposit. The effect is of the order of a ten per cent loss of current efficiency for 10 mg/L. Generally the concentration should be kept below 0.1 mg/L and control is achieved by cementation with zinc dust. Nickel is removed with cobalt and it is cobalt that determines the conditions for that removal step. Hence nickel is usually adequately controlled.

Potassium and Sodium

These elements have no impact on electrode processes. As for magnesium, their presence in solution will reduce the capacity of the solution to hold zinc and will raise solution density and viscosity, consequently raising cell voltage and possibly impeding settling and filtration operations. However, sodium and potassium jarosites are readily formed, particularly if iron separation is at elevated temperatures following hot acid leaching. In this case, the levels of these elements will normally be controlled at low concentrations. Otherwise a solution bleed would be necessary to maintain circuit control.

Selenium

Selenium can cause severe loss of current efficiency and resolution of the zinc deposit, particularly on the inner cathode surface. Levels should be maintained below 0.01 mg/L, but are readily held below these levels by zinc dust purification. Selenium is effectively separated from calcines by volatilisation during the roasting operation.

Silica

Silica forms zinc silicate during the roasting operation. Zinc silicate is dissolved during acid leaching below pH 4.0 to give unstable silica in solution, which can precipitate as a gel interfering with settling and filtration operations. If silica is high in zinc concentrates, particular conditions need to be used in leaching to enable it to be precipitated in a manageable form (see Chapter 5). Inadequate handling of silica can have serious effects on zinc losses in leach residues as well as restricting production due to settling and filtration constraints. Otherwise, silica is unlikely to get through to electrolysis and will have no impact on electrode reactions.

Tellurium

Tellurium is a particularly harmful element to zinc electrodeposition and levels should be below 0.005 mg/L. Tellurium is removed during iron precipitation, but is uncommon and normally only related to mineral deposits with a large copper association.

Thallium

Thallium has no impact on the electrode reactions, however it can raise the level of lead in the zinc deposit and will co-deposit with zinc. The SHG specification for thallium is 0.001 per cent, requiring less than 1 mg/L in purified solution. As indicated earlier, thallium tends to follow cadmium and concentrates in the cadmium circuit where it can be removed by permanganate precipitation. Otherwise thallium will be precipitated in the iron removal stage provided it is fully oxidised to the trivalent state.

Tin

Tin has a severe effect on current efficiency with a loss of 50 per cent for 1 mg/L. It also affects the morphology of the zinc deposit. Fortunately tin can be adequately controlled by zinc dust cementation.

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Electrolysis

PROCESS PRINCIPLES

Basic Electrochemical Reactions

The electrodeposition of zinc involves the discharge of zinc ions from a zinc sulfate solution at a cathode of a simple open electrolytic cell. Water is decomposed at the anode to release oxygen, to form hydrogen ions and to release electrons. There are a number of competing reactions at the cathode involving the possible discharge of other metal ions in solution and in particular the discharge of hydrogen ions to release hydrogen (see Equations 7.1 to 7.3). The cathode reaction which predominates is highly sensitive to solution purity, particularly the competition between zinc and hydrogen deposition, and it was this fact that was the major impediment to the initial development of the electrolytic zinc process.



The particular sensitivity can be illustrated by examining standard electrode potentials for a number of electrode reactions as given in Table 7.1. Zinc has a more negative standard electrode potential (or is less noble) than hydrogen, indicating that hydrogen ions should be discharged at the cathode in preference to zinc, and suggesting that electrodeposition of zinc from an aqueous solution should not be possible. However these potentials apply under reversible conditions at no current flow when forward and reverse reactions are in equilibrium. They provide information on the thermodynamic possibility of the reaction proceeding, not on the rate at which the reaction proceeds. There are a number of factors which restrict the reaction at the electrode surface, as indicated by the electrical current flow, and these restrictions may be overcome by increasing the applied electrode voltage. The increased potential required above the reversible electrode potential is termed the overvoltage (or overpotential).

At operating conditions for zinc electrowinning, the overpotential for hydrogen deposition on the zinc surface is sufficiently high to effectively raise the potential above that for zinc deposition, limiting Equation 7.2 in favour of Equation 7.1. Other metal surfaces can have quite different hydrogen deposition overpotentials from zinc. If impurity metals are codeposited with zinc in accordance with Equation 7.3, they can act as sites of reduced hydrogen overpotential, shifting the system in favour of hydrogen and reducing the efficiency with which electric current is used for zinc deposition. The efficiency and indeed success of the zinc electrowinning operation therefore critically depends on control of factors affecting electrode overpotentials and understanding the principles involved. These issues are examined in greater depth in the following sections of this chapter.

Faraday's Law for electrodeposition may be expressed as:

$$m = \frac{ItM}{nF} \quad (7.4)$$

where:

m is the mass deposited in grams

I is the current passed in amps
 t is the time of passage of the current in seconds
 M is the molecular weight of the material deposited
 n is the number of electrons involved per mole
 F is the Faraday constant = 96 500 coulombs per mole

From the above expression and for the deposition of one kilogram of zinc 820.0 amp hours (It) are theoretically required. For hydrogen 26 590 amp hours are required per kg.

The efficiency with which electric current is used for the deposition of zinc is an important economic parameter. For the deposition of m kg in t hours per cell, the theoretical current required is: $\frac{820m}{It}$ amps, and the 'Current Efficiency' with a total current of I amps is $\frac{820m}{It} \cdot 100$ per cent. The

remaining current is largely used for the deposition of hydrogen.

Thermodynamics and Kinetics of Electrode Reactions

If an electrode is in a state of equilibrium between the surface and the solution, it is termed reversible and there will be no change in electrode potential with applied current. Whereas if electrode reactions are slow and influenced by energy barriers to the attainment of equilibrium, they are termed irreversible and there will be an increase in potential as the current is increased.

For a reversible electrode the equilibrium discharge potential for metal ions in contact with the metal may be expressed as:

$$E = E^0 + \frac{RT}{nF} * \ln(a) \quad (7.5)$$

where:

E^0 is the electrode potential under standard conditions
 R is the Universal Gas Constant (8.314 joules K⁻¹ mole⁻¹)
 T is the temperature in °K
 a is the ionic activity of the metal ion in solution = molar concentration × mean ion activity coefficient (which is dependent on solution composition and the ionic strength of the solution)
 F is Faraday constant = 96 500 coulombs per mole
 n is the number of electrons involved per mole

TABLE 7.1

Standard electrode potentials (relative to the H⁺ electrode at 25°C).

Electrode Reaction	E ⁰ volts
Au ²⁺ / Au ⁰	+1.42
Cl ² / Cl ⁻	+1.36
Hg ²⁺ / Hg ⁰	+0.85
Ag ⁺ / Ag ⁰	+0.80
Fe ³⁺ / Fe ²⁺	+0.77
Sb ⁵⁺ / Sb ³⁺	+0.75
As ⁵⁺ / As ³⁺	+0.58
O ² / OH ⁻	+0.40
Cu ²⁺ / Cu ⁰	+0.34
As ³⁺ / As ⁰	+0.30
Sb ³⁺ / Sb ⁰	+0.10
H ⁺ / H ⁰	0
Pb ²⁺ / Pb ⁰	-0.13
Sn ²⁺ / Sn ⁰	-0.14
Ni ²⁺ / Ni ⁰	-0.25
Co ²⁺ / Co ⁰	-0.28
In ³⁺ / In ⁰	-0.34
Cd ²⁺ / Cd ⁰	-0.41
Fe ²⁺ / Fe ⁰	-0.44
Ga ³⁺ / Ga ⁰	-0.56
Zn ²⁺ / Zn ⁰	-0.76
Mn ²⁺ / Mn ⁰	-1.10
Al ³⁺ / Al ⁰	-1.66
Mg ²⁺ / Mg ⁰	-2.39

E^0 values are given for various metals at 25°C relative to the standard hydrogen electrode in Table 7.1.

Equation 7.5 may be expressed as:

$$E = E^0 + 19.8 \cdot 10^{-5} \cdot (T/n) \cdot \log_{10}(a) \quad (7.6)$$

or for zinc:

$$E_{Zn} = -0.763 + 9.90 \cdot 10^{-5} \cdot T \cdot \log_{10}(\gamma_{Zn} \cdot C_{Zn}) \quad (7.7)$$

where:

γ_{Zn} is the activity coefficient for zinc in solution

C_{Zn} is the concentration of zinc in solution in gram moles per litre

and for hydrogen:

$$\begin{aligned} E_H &= E^0 + 9.90 \cdot 10^{-5} \cdot T \cdot \log_{10}(a_H^2/p_{H_2}) \\ &= 0.059 \cdot \log_{10}(a_H) \text{ at } 25^\circ\text{C} \\ &= 0.059 \cdot pH \quad (7.8) \end{aligned}$$

where:

a_H is the activity of hydrogen ions in solution

p_{H_2} is the partial pressure of hydrogen taken as one atmosphere

In the practical situation electrodes depart from equilibrium and for the electrode process to proceed at a practical rate, a higher potential than the equilibrium value is needed to overcome the energy loss in activating ions taking part in the reaction and in transporting ions to the electrode surface.

The actual observed electrode potential for an operating cell is then:

$$E_a = E + \eta_a + \eta_c \quad (7.9)$$

where:

E is the reversible potential as defined above

η_a is the activation overpotential (or chemical polarisation)

η_c is the concentration overpotential (or concentration polarisation)

The activation overpotential may be collectively made up of three broad processes:

- the energy required to decompose complex ions in solution,
- the energy barrier to be overcome to discharge the ion, and
- the energy required to arrange the metal on the electrode surface in a particular crystalline state.

The concentration overpotential normally has little impact until high currents are reached and depends on boundary layer effects as influenced by the degree of agitation of the solution, eventually limiting the current to a level determined by ionic diffusion.

Activation Overpotential

Chemical activation processes are described by the Arrhenius equation:

$$k = A \exp\left(-\frac{G_a}{RT}\right) \quad (7.10)$$

where:

G_a is the activation energy

A is a constant

k is the specific reaction rate constant (Rate = $k \times$ concentration)

For an electrode reaction a similar relationship applies:

$$j = A \exp \left(-\frac{G_a + n\beta\eta F}{RT} \right) \quad (7.11)$$

where:

G_a is the equilibrium activation energy

n is the number of electrons involved

β is a constant termed the transfer coefficient

η is the overpotential

j is the current density

This may be expanded to $j = A \exp \left(-\frac{G_a}{RT} \right) * \exp \left(-\frac{n\beta\eta F}{RT} \right)$. When the overpotential (η) is zero the current flowing is termed the exchange current (j_o) applying at the reversible potential or

$$j_o = A \exp \left(-\frac{G_a}{RT} \right)$$

Hence:

$$j = j_o \exp \left(-\frac{n\beta\eta F}{RT} \right) \quad (7.12)$$

or by rearrangement:

$$\eta = \frac{2.303 * RT * (\log j_o - \log j)}{n\beta F} \quad (7.13)$$

Equation 7.13 is known as the Tafel relationship $\eta = a + b * \log (j)$

with a Tafel intercept $a = 2.303 \frac{RT}{n\beta F} * \log (j_o)$

and a Tafel slope $b = - 2.303 \frac{RT}{n\beta F}$

The transfer coefficient (β) is a function of the arrangement of molecules within the electrode/electrolyte interface layer. The transfer of ions across this layer is influenced by the species present, their structure and their concentration.

The exchange current (j_o) expresses the magnitude of equal and opposite currents flowing at equilibrium (ie for anodic and cathodic reactions). Both currents are equal giving no net current flow.

Reversible electrodes generally have high exchange currents and low Tafel slopes. Irreversible electrodes are characterised by low exchange currents and high Tafel slopes. These characteristics apply to both anodic and cathodic reactions and may be illustrated in Figure 7.1.

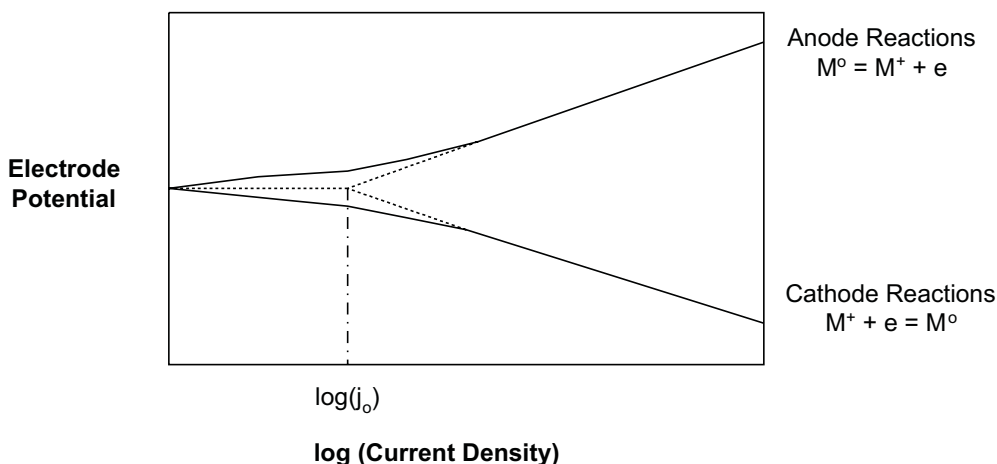


FIG 7.1 - Exchange currents for an electrode reaction.

The Tafel relationship applies at high current densities but fails at low current densities as shown in Figure 7.1. The exchange current can be found from the intersection of the projected Tafel line with the equilibrium electrode potential.

Concentration Overvoltage

As electrolysis proceeds, zinc ions will be depleted at the electrode surface and will require diffusion from the bulk of the solution across a stagnant boundary layer to replace zinc ions discharged and deposited at the cathode surface. The cathode current will equate to the diffusion rate according to Equation 7.14.

$$j = \frac{nFD_z(C_B - C_s)}{\delta} \quad (7.14)$$

where:

D_z is the diffusion coefficient for zinc ($0.5 \times 10^{-5} \text{ cm}^2/\text{sec}$)

C_B is the bulk solution concentration of zinc

C_s is the zinc concentration at the electrode surface.

δ is the thickness of the boundary layer

In the extreme, where the process is limited by diffusion, $C_s = 0$ and the current is limited to:

$$j_{LIM} = \frac{nFD_z C_B}{\delta} \quad (7.15)$$

In commercial practice it is noted that limiting currents where zinc deposition rate diminishes is of the order of 1000 amps/m^2 , for a concentration of around 0.75 moles/L and gives a boundary layer thickness of:

$$\begin{aligned} \delta &= 2 \times 96,487 \times 0.5 \times 10^{-9} \times 750 / 1000 \\ &= 7.2 \times 10^{-5} \text{ m. or } 0.07 \text{ mm} \end{aligned}$$

This is of course a simplification, but illustrates the importance of boundary layer conditions and the concept of a limiting current. The thickness of the boundary (diffusion) layer is determined by solution

viscosity and by the ionic species present in solution. It can be reduced by turbulence due to the generation of gas at the electrode surface. In the case of the anode, oxygen is the principal product and its evolution creates considerable turbulence in the surface layer. Similarly at the cathode, the generation of hydrogen accounts for approximately seven to ten per cent of the current passed. Hydrogen bubbles form and grow and when liberated form a void in the diffusion layer, which is filled by bulk solution. This is a particularly effective method of mixing and produces a relatively thin diffusion layer – of the order of 0.1 mm as indicated above. Some hydrogen generation at the cathode is therefore quite beneficial. Clearly, high solution flows at the electrode surface will also reduce the boundary layer and enable high current densities to be achieved.

The effect of the slow diffusion of zinc to the electrode surface and the depletion of the surface concentration to C_s gives rise to a change in electrode potential from that applying to the bulk of the electrolyte at concentration C_B , or gives rise to a concentration overvoltage (η_c). In accordance with Equation 7.5 this may be expressed as:

$$\eta_c = \frac{RT}{nF} * \ln(C_s) - \frac{RT}{nF} * \ln(C_B)$$

$$= - \frac{RT}{nF} * \ln\left(\frac{C_B}{C_s}\right)$$

Using Equations 7.14 and 7.15 this may be simplified to:

$$\eta_c = \frac{RT}{nF} * \ln\left(\frac{(j_{LIM} - j)}{j_{LIM}}\right) \quad (7.16)$$

Electrolytic Cell Current – Voltage Relationship

Applying the basic principles of overvoltages and limiting currents to an operating cell gives the voltage-current relationship for the total cell as shown in Figure 7.2. The effect of a change in zinc concentration will shift the cathode curves as illustrated in Figure 7.3.

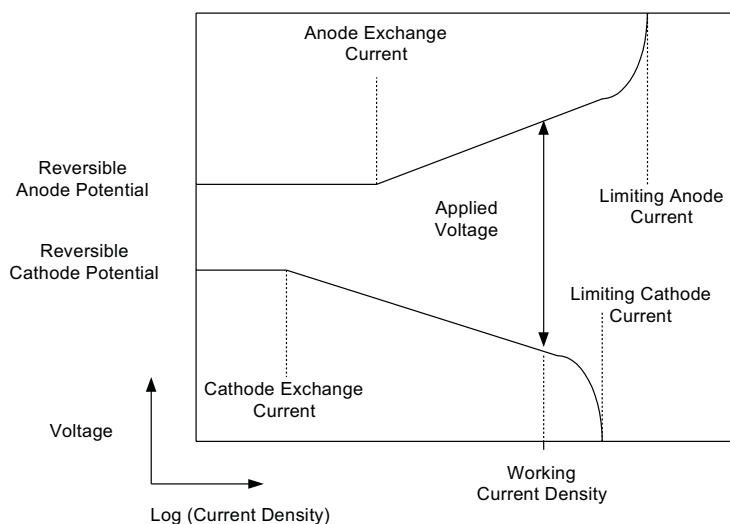


FIG 7.2 - Operating cell – current/voltage relationships.

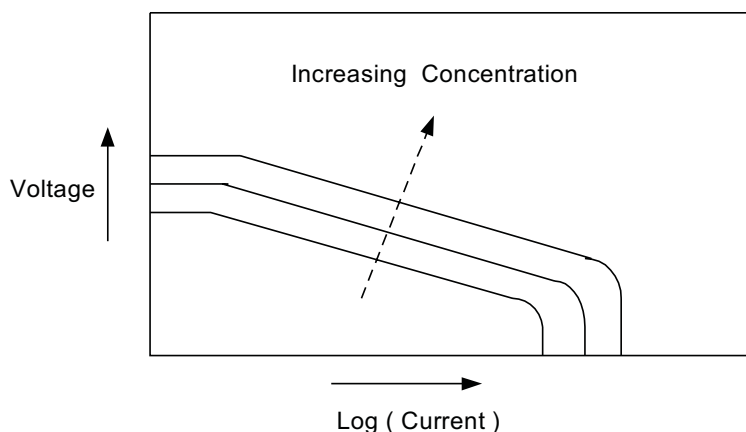


FIG 7.3 - Effect of concentration on current/voltage relationship for the cathode reaction.

CATHODE REACTIONS

The above principles apply equally to zinc and hydrogen, and the key to practical operation is the relative values of overvoltage for both competing elements.

Zinc Deposition

As shown in Table 7.1 the standard reversible electrode potential for zinc is $E^0 = -0.763$ V, and for practical operating conditions with an electrolyte containing 50 g/L zinc and 150 g/L sulfuric acid, Equation 7.7 gives a reversible electrode potential of close to -0.81 V. With practical operation at a current density of 400 amps/m^2 the overvoltage is measured in the range of 0.05 to 0.12 V, giving a mean cathode potential of -0.895 V.

The exchange current density for zinc deposition on a zinc surface is reported at $1.26 \times 10^{-4} \text{ amps/m}^2$ ($\log(j_0) = -3.9$) (Fisher-Bartelk, 1960).

Hydrogen Deposition

For an acidity of 150 g/L sulfuric acid (1.53 moles/L) and for an assumed activity coefficient of 0.8 , Equation 7.8 indicates a reversible electrode potential of $+0.005$ V. The hydrogen overvoltage on zinc may be defined according to the parameters for the Tafel equation for a 2N sulfuric acid solution (98 g/L) as shown in Table 7.2. Hence for normal operating conditions at 38°C and a current density of 400 amps/m^2 , the activation overvoltage for hydrogen is -1.109 V and the electrode potential is -1.104 V.

TABLE 7.2

Tafel constants and limiting current for hydrogen deposition on zinc.

Temperature $^\circ\text{C}$	20	40	60	80
a (volts)	0.705	0.735	0.765	0.767
b (volts)	0.163	0.143	0.117	0.108
j^0 ($\text{amps/m}^2 \times 10^{-4}$)	0.464	7.34	29.4	28.3

The overall electrode potential for deposition of hydrogen at -1.1 V is more negative than the potential for the deposition of zinc, hence zinc will preferentially deposit. At different deposition currents the corresponding potentials are as given in Table 7.3.

TABLE 7.3*Electrode potentials for zinc and hydrogen deposition as a function of current (at 38°C).*

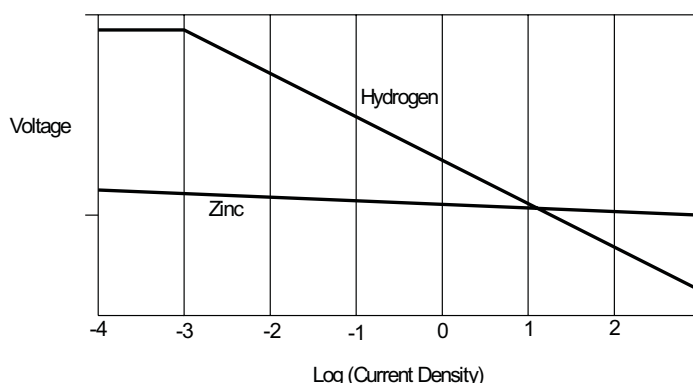
Current density amps/m ²	0.1	1.0	10	100	400
Zinc deposition potential (volts)	-0.827	-0.846	-0.865	-0.884	-0.895
Hydrogen deposition potential (volts)	-0.582	-0.727	-0.872	-1.017	-1.104

This behaviour is illustrated in Figure 7.4 and shows that at low current densities hydrogen will preferentially be deposited and at higher current densities zinc deposition will be preferred due to the larger change in the hydrogen overvoltage. The cross over point represents the critical current density for commencement of zinc deposition and in the illustration is around 10 amps/m², but varies depending on the composition of the electrolyte.

At a given applied potential, the respective currents for simultaneous zinc and hydrogen deposition can be indicated. The total current will be the sum of these two currents and the proportion of total current used for zinc deposition is the ‘current efficiency’, which may be expressed as:

$$\text{Current efficiency} = \text{CE} = j_{\text{zinc}} * 100 / (j_{\text{zinc}} + j_{\text{hydrogen}})$$

$$\text{or} = (j_{\text{total}} - j_{\text{hydrogen}}) * 100 / j_{\text{total}}$$

**FIG 7.4 - Electrode potential – current relationship for zinc and hydrogen.**

For the above data at a zinc deposition current density of 400 amps/m² the electrode potential is 0.895 V and the corresponding hydrogen current density is 14 amps/m². This suggests a current efficiency of 96.6 per cent, based solely on the activation overvoltage.

However at practical current densities the concentration overvoltage is also of importance and is given in Equation 7.16 in terms of the limiting current density. The limiting current density is determined by Equation 7.15. The diffusion coefficient for hydrogen ions is around five times higher than for zinc so that the limiting current for hydrogen deposition is unlikely to come into effect within the practical operating range for zinc deposition. For Figure 7.4, at a zinc deposition current of 400 amps/m², this would add a concentration overvoltage of approximately 0.015 V to give a total zinc deposition potential of 0.91 V. At this applied potential, the hydrogen current density from Table 7.3 would be 18.5 amps/m² and the calculated current efficiency would be 95.6 per cent.

The impact of the concentration overpotential effect on the current – voltage curves are illustrated in Figure 7.5. On the basis of the calculation method for current efficiency used above, Figure 7.5 indicates that the current efficiency will rise to a maximum as the current increases and then decline as

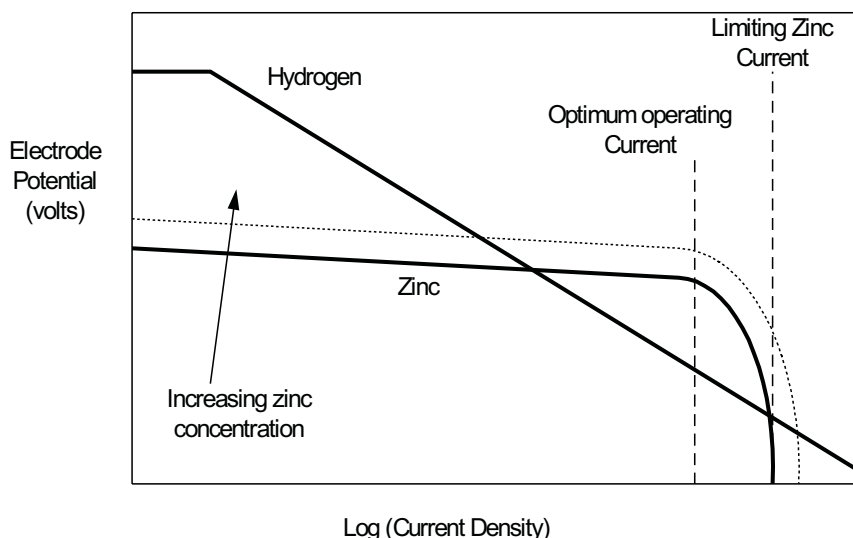


FIG 7.5 - Electrode potential – current relationships for zinc and hydrogen. Showing limiting current and concentration effects.

the limiting diffusion current for zinc is approached. This will also clearly be influenced by the concentration of zinc in solution, and the maximum will be greater and occur at higher current densities as the concentration of zinc is increased.

Effect of Changes in Electrolyte Composition

The effect of change in the zinc concentration is illustrated above, and clearly the hydrogen curve will also be raised by an increase in the hydrogen ion concentration. If both the zinc and acid concentrations are changed by the same relative molar concentrations, both the zinc and hydrogen curves in Figure 7.5 will shift by the same relative amount and the current efficiency will remain unchanged. This has been empirically expressed as Wark's Law (Wark, 1963).

$$\text{Current Efficiency} = \text{CE} = \frac{WR}{(1 + WR)} \quad (7.17)$$

where:

R is the zinc to sulfuric acid concentration ratio in g/L

W is a constant dependent on the purity of the solution, commonly approximately 30

This rule is an approximation within a narrow band of operating conditions but is useful in emphasizing the importance of control of the zinc to acid ratio in practical operation, and in quantifying the effect of such changes by establishing an empirical 'Wark's constant'.

Effect of Changes in Temperature

For a given current density, the zinc electrode potential increases with temperature in accordance with Equations 7.5 and 7.13, although the contribution of overvoltage is minor. For competing hydrogen deposition the effect on overvoltage is much greater and decreases with a rise in temperature. The overall effect of a temperature increase is to favour hydrogen deposition and thus decrease the current efficiency for zinc deposition.

On the other hand, increasing the temperature also increases the electrical conductivity of the electrolyte and decreases the potential drop through the electrolyte, reducing energy consumption. Thus there is an optimum operating temperature to balance these two opposing effects and give a minimum energy consumption per unit of zinc deposited.

For solutions containing impurities that reduce hydrogen overvoltage, the effect of temperature is more pronounced and a lower optimum temperature is required. Generally the optimum temperature range is between 36 and 46°C, but the higher the purity of the electrolyte the higher the optimum operating temperature will be.

Effect of Impurities on the Cathode Process

Minor metals in solution with electrode potentials more negative than zinc will compete with zinc for deposition in the same way as for hydrogen as illustrated in Figures 7.4 and 7.5. Co-deposition can be limited or avoided by reducing electrode potentials through a reduction in the concentration of the impurities to sufficiently low levels (in accordance with Equation 7.5). Alternatively, the overvoltage can be raised in accordance with Equation 7.13 by raising the current density. The latter action can be particularly effective if the limiting current for that impurity can be exceeded (Equation 7.15).

The most significant issue relating to deposited impurities is the hydrogen overvoltage for deposition on that impurity. If this is low, then hydrogen can be released at the impurity site and zinc will not be deposited. The impurity will also set up a local corrosion cell in which the impurity serves as a cathode and the adjacent zinc acts as an anode, which will dissolve with release of hydrogen at the impurity cathode, unless the hydrogen overvoltage can be raised sufficiently by the applied current.

The hydrogen overvoltage on impurity elements is thus of major significance. Table 7.4 lists typical data on hydrogen overvoltages at normal operating current densities.

It is of interest that iron has a relatively low hydrogen overvoltage. However the overpotential for deposition of iron on zinc is high and prevents the presence of iron within the zinc deposit.

Aluminium has a relatively high hydrogen overvoltage and is therefore suitable for use as an initial or starter cathode material onto which zinc can be deposited.

An impurity element may deposit in elemental form or in the form of an alloy with zinc. If sufficient impurity element can be deposited in one location to significantly reduce the hydrogen overvoltage, this will result in the formation of an active site with the evolution of hydrogen in copious amounts. A consequence of this is that further deposition of impurities at that site will be impeded, which will lead to the formation of other active sites and a progressive deterioration of current efficiency for zinc deposition with time. Zinc current efficiency can therefore be expected to decrease with deposition time.

As the current density is increased, the overvoltage for hydrogen deposition generally increases at a faster rate than for zinc deposition to the point where zinc deposition on the impurity element can occur in preference to hydrogen. When this occurs, the active site for hydrogen generation can be sealed and the effect of the impurity on zinc current efficiency can be eliminated. There will be a critical current

TABLE 7.4

Hydrogen overvoltage on impurity elements.

Element	Volts at 400 amps/m ²
Zinc	1.1
Lead	1.2
Aluminium	0.9
Cadmium	0.85
Tin	0.79
Antimony	0.79
Germanium	0.75
Copper	0.68
Iron	0.55
Cobalt	0.48
Nickel	0.47
Gold	0.45
Platinum	0.1

density for each impurity element at which this occurs. However, most of these will be beyond the limiting current density for zinc deposition and are thus outside any practical operating range.

The formation of a corrosion cell by a deposited metal impurity is determined by the differences in standard electrode potentials for the metals and their respective hydrogen overvoltages. High corrosion rates are favoured by large differences in standard electrode potentials (from Table 7.1 – Sb, Cu, As, Ge) and by those metals with low hydrogen overvoltages (Table 7.4 - Co and Ni). However the formation of active sites from concentrated deposition of impurities is favoured by those impurities that are difficult to deposit and with standard potentials close to zinc – such as Co and Ni. Whereas those impurities, which have large differences in standard electrode potentials from zinc, tend to be more widely distributed and lead to more uniform corrosion.

As mentioned, it is likely that many impurities deposit as alloys with zinc but can be concentrated into more active sites for hydrogen evolution by re-solution of associated zinc, leaving the impurity metal. For localised active sites, the effects of re-solution of the deposit by these mechanisms takes place at regions of lower current density and can aggravate the non-uniformity and pitting of the deposit. Deposition time also extends these effects and leads to declining current efficiency as indicated above.

To add further complications, the effects of a number of impurities may be synergistic, enhancing the effects of individual elements alone. This may be caused by co-deposition or by the formation of alloys with reduced hydrogen overvoltages.

Cathode Deposit Morphology

The crystalline structure of electrochemically deposited zinc is usually as hexagonal platelets, which tend to grow in stacks. As indicated earlier in this chapter, part of the activation overvoltage for zinc deposition is the energy required to arrange the metal in a particular crystalline state. When metals are deposited at or near equilibrium conditions (that is at low current density and high metal availability at the electrode surface), crystals will be large and the growth of crystal faces where the energy of incorporation of the atom is lowest will be favoured. For zinc, this structure tends to be flat hexagonal platelets aligned parallel to the electrode surface. When deposition occurs at or near the limiting current density, the crystal size is much smaller and growth of higher energy planes is favoured. Under these conditions, the zinc platelets tend to be oriented at 90° to the electrode surface and are tightly packed. Extension to form dendrites can occur. At intermediate current densities, platelet orientation tends to be more random.

Four general types of deposit morphology can be defined. The first (at low current densities) corresponds with flat platelet orientation and can be irregular and lumpy. In the second case, the orientation of the platelets changes and the deposit becomes more compact, but can often show a pinholed appearance. The third classification is represented by a random orientation giving a highly compact and relatively even deposit, which is the one preferred as the most manageable. The fourth or extreme type is the tightly packed structure with 90° orientation and a more irregular surface (Winand, 1992).

The transition from one deposit type to another can be related to the deposition overvoltage (or degree of polarisation). This of course increases with current density, and is influenced by the strength and composition of the electrolyte, impurities present and temperature, but can also be controlled by the addition of reagents to the electrolyte. Reagents most commonly used for this purpose are a combination of gelatin glue and antimony – added as potassium antimonial tartrate. The effect of glue is to raise overvoltage, balanced by antimony with the opposite effect. The aim is to optimise the zinc deposition overvoltage under tight control and in favour of the formation of the third type of uniform and smooth deposit.

The formation of nodular deposits can be a particular practical concern due to the tendency to cause electrical shorting between cathode and anode, as well as causing problems in cathode stripping. Nodule formation is aggravated by a high degree of cathode polarisation and particularly by high solution molarity or total dissolved salt content. There is also evidence to suggest that nodular deposits can be initiated by the presence of particulate material in suspension in the electrolyte – such as gypsum or other precipitated salts, which can adhere to the surface of the cathode and initiate the formation of a nodule. Salt precipitation will of course be promoted in high molarity solutions.

An irregular and nodular deposit will have a greater surface area than a smooth deposit and hence the actual deposition current density will be lowered. This in turn can shift the cathode reaction potentials to increase hydrogen deposition and hence reduce current efficiency.

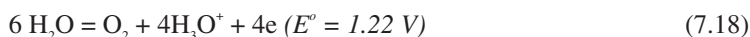
Zinc Cathode Stripping

In the industrial electrolytic zinc process, the initial starting cathode is an aluminium sheet onto which the zinc is deposited. When it has reached a suitable thickness, the zinc deposit is stripped from the aluminium and the process is repeated. The nature of the aluminium cathode as well as the zinc deposit is important in allowing the zinc deposit to readily separate or be stripped from the aluminium. Aluminium alloys with 500 ppm titanium are used to improve this performance and the level of fluorine in solution is quite critical. Generally levels of fluorine above 15 mg/L can cause stripping problems but the levels can be higher without impact if the fluoride is complexed, such as with aluminium in solution. Regular brushing of the aluminium sheet assists in improving stripping performance.

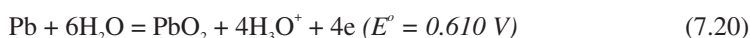
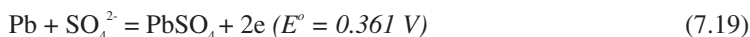
The nature of the zinc deposit can impede stripping if it lacks a rigid coherent structure and is porous and irregular, such that it fractures easily when stripping is attempted. This will tend to leave remnants attached to the aluminium and if returned to the cells can cause excessive localised growth and short circuiting between the cathode and anode. Also fragmentation of the zinc sheet on separation will cause high losses with potential to jam the stripping equipment. In extreme situations, particularly when the zinc deposit is fragile and cannot be removed as a single sheet, it is necessary to pickle the cathodes in spent electrolyte and dissolve off any residual zinc.

ANODE REACTIONS

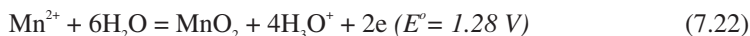
The principle reaction at the anode is the decomposition of water resulting in the formation of oxygen and sulfuric acid according to the Equation 7.18.

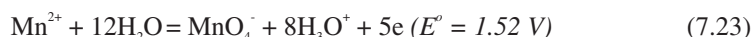


The surface of the lead anode is oxidised and passivated by the reactions given in Equations 7.19, 7.20 and 7.21, which coat the anode surface with lead dioxide.



In addition, manganese in solution is also oxidised to permanganate and manganese dioxide according to Equations 7.22 and 7.23.





Both PbO_2 and MnO_2 are electrically conductive, and hence the principal reaction of oxygen release occurs at the solution-coating interface. The activation overpotential for oxygen on the combined $\text{PbO}_2 - \text{MnO}_2$ surface is approximately 0.84 V, giving an operating anode potential of around 2.0 V for Equation 7.18, hence most of the above reactions can also proceed. The coating itself imposes a growing electrical resistance, which can give a potential drop of 0.2 V.

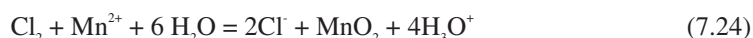
Permanganate can be reduced in solution by Mn^{2+} to form MnO_2 in suspension, giving rise to 'cell mud'. The amount of MnO_2 formed relates to the relative current used for its formation compared with the current used for oxygen evolution (or current efficiency). This is particularly dependent on the overvoltage for oxygen evolution on the anode surface, which changes with time as the scale develops. For a fresh new lead surface, the current efficiency for manganese dioxide deposition is high but reduces to near one per cent after 30 days of operation. The formation of MnO_2 is increased at higher cell temperature, but is decreased by higher acidity, current density and the time interval between anode cleaning.

Lead Anode Corrosion

Prior to the build-up of the anode surface coating, the corrosion rate of the lead anode is relatively high. This corrosion supplies lead ions to the electrolyte, which can then co-deposit with zinc on the cathode, contaminating the product zinc metal. This effect diminishes with the age of the anode and suitably low levels of lead in zinc can be achieved, although often assisted by the addition of strontium carbonate to the electrolyte.

Because of the lead contamination effect and high rate of formation of MnO_2 on new anodes, it is often the practice to pre-treat the anodes in special cells prior to use in the main production cells. Pretreatment may include the use of an acid solution rich in manganese (usually permanganate) or in solutions high in fluoride, which promote the formation of PbO_2 .

Of the impurities that cause anode corrosion, chloride is the most severe. Chlorine gas is formed at the anode as well as chlorate and perchlorate ions. Chlorine and chlorate react readily with manganese in solution to form manganese dioxide according to Equation 7.24, and only perchlorate and chloride appear to persist in solution.



If the chloride level in solution is above 400 mg/L, then chlorine evolution from the cells with oxygen can become noticeable and be a hazard to personnel. Chlorine evolution is considerably increased with new lead anodes.

The role of fluoride in anode corrosion is not clear since chloride generally predominates. The main effect of fluoride is on the corrosion of the cathode surface and its role in causing sticking of the zinc deposit to the aluminium cathode.

To minimise the corrosion of the lead anode it is normally alloyed with between 0.5 and 1.75 per cent silver for improved corrosion resistance. Calcium-lead alloys are used in the copper industry but have only slowly found favour for zinc applications, largely due to the difficulties associated with re-melting for anode recycle, and control of the calcium content. Calcium alloyed anodes as rolled sheet are preferred for large electrodes, where the added rigidity and strength are a significant advantage.

Alternative anode materials include titanium, usually with a rhenium oxide coating to lower oxygen overvoltage, marketed as a Dimensionally Stable Anode (DSA). Oxygen overvoltage is reduced by about 0.4 V, which is quite significant. Titanium anodes will not tolerate scaling by MnO_2 and it is necessary to have solutions relatively free of manganese. This is hard to achieve, given the fact that manganese is a common component of sulfide zinc concentrates and there are no practical procedures

for ready separation of manganese from leach solutions, other than solvent extraction with its inherent complications. In fact, the formation of MnO_2 at the anode of a normal electrowinning cell is the primary means of control and elimination of manganese. Otherwise a solution discard procedure would be necessary, but would not control manganese to the low levels required for DSA anodes.

Overvoltage Reduction

The oxygen overvoltage is a significant component of the cell voltage and energy consumption. In order to reduce the anode overvoltage, the use of de-polarisers has been attempted. Methanol or ethanol can be added to solution and are oxidised at the anode at lower anode potential. This is effective but generally the cost of the alcohol added exceeds the cost of power saved. Similarly, the use of hydrogen distributed through porous anodes was tried at Ruhr Zinc but again it was difficult to justify the added complexity and cost of hydrogen supply. Similarly, SO_2 can be added to solution, but generates an additional mole of sulfuric acid for each mole of zinc deposited and must be removed from the spent electrolyte, usually as gypsum. Otherwise, different types of anodes can be used such as DSA but must be able to handle the issues associated with manganese.

ELECTROLYTE CONDUCTIVITY

The voltage drop due to the electrical resistance of the electrolyte is a significant component of the total cell voltage and needs to be understood and minimised. Electrolyte conductivity is increased by raising the acidity and the temperature of the electrolyte, and is decreased by increasing metal ion concentrations – particularly zinc, manganese and magnesium.

Acidity should be kept as high as possible commensurate with requirements for zinc deposition current efficiency and recognising the need to maintain an optimum zinc to acid ratio. Temperature also has a contrary effect on current efficiency due to the impact on hydrogen overvoltage and the effects of impurities, and an optimum balance is necessary at around 40°C.

Because of its low atomic weight, magnesium can have a relatively high molar concentration and accordingly has the greatest impact of all metal impurities in solution on reducing conductivity as well as increasing solution viscosity. Magnesium needs to be maintained at minimum levels for this reason.

An expression for the conductivity or specific conductance of the electrolyte (in $\text{ohm}^{-1}.\text{cm}^{-1}$) has been given by Tozawa *et al* (1993), and is shown in Equation 7.25.

$$K = 0.004 + 0.00115 t + 0.0028 [H_2SO_4]t + 0.00114 [M]t + 0.3442 [H_2SO_4] - 0.0451 [H_2SO_4]^2 - 0.1058 [H_2SO_4].[M] - 0.022[M] + 0.0286 [M]^2 \quad (7.25)$$

where:

$[M]$ is the molar concentration of cations in solution as (Zn + Mg + Mn + 0.39Na + 0.23K)
 $[H_2SO_4]$ is the moles/L of sulfuric acid in solution
 t is the temperature in °C

The voltage drop through the solution is then equal to $\frac{j l}{K}$ where j is the current density in $\text{amps}.\text{cm}^{-2}$ and l is the interface distance in cm between anode and cathode surfaces (normally around 3.5 cm), and K is the specific conductance of the electrolyte in $\text{ohm}^{-1}.\text{cm}^{-1}$ as calculated by Equation 7.25.

Decreasing the electrode spacing will reduce the solution path resistance and hence voltage drop, but requires flat electrodes, the absence of dendritic growth, and careful alignment of the electrodes. The spacing must allow room for the zinc deposit to grow. There are practical limits to these factors, which generally determine that electrode separation distance is of the order of 30 to 40 mm (centreline

distances), and the pitch from cathode to cathode is in the range of 60 to 80 mm. Reduced spacing is easier to manage with smaller electrode areas.

Mixing of the electrolyte within the cell is also an important issue, as depletion of zinc in a stagnant layer close to the cathode surface will reduce the conductivity in that area and raise the cell voltage. The evolution of gas from the electrodes greatly assists in mixing solution between the electrodes and indeed also reduces the thickness of the solution boundary layer at the electrode surface and allows the limiting current to be raised. Forced circulation of the electrolyte with highly turbulent flow can significantly raise the limiting current and practical operating current densities (see Process Principles at the start of this chapter).

ZINC CELL PERFORMANCE

Cell Voltage and Power Consumption

The voltage component of a typical zinc electrowinning cell operating at a current density of 400 amps/m² is of the order of 3.2 to 3.4 V. The various components of that voltage for an operating plant at 500 amps/m² are summarised in Table 7.5. This data applies to a mean temperature of 38°C and a spent electrolyte acidity of 160 g/L.

TABLE 7.5
Components of cell voltage (Bratt, 1977).

Cathode	Reversible potential	820 mV
	Activation potential	60 mV
	Effect of smoothing additives	2 mV
Anode	Reversible potential	1217 mV
	Oxygen overpotential	840 mV
	Scale effects	150 mV
	Additive effects	45 mV
	Silver alloy effect (0.5%)	- 80 mV
	Manganese effect	-190 mV
Conductivity - IR drop	Cathode sheet	2 mV
	Anode sheet	10 mV
	Contacts	24 mV
	Electrolyte potential drop	450 mV
	Gas bubble effect (10% of electrolyte)	45 mV
Total cell voltage		3395 mV

From the subdivision shown in Table 7.5, the anode electrode potential and oxygen overvoltage are clearly major factors, representing 60 per cent of the cell voltage and hence power consumption. With the oxygen overvoltage equal to almost 25 per cent of the total there is considerable opportunity for power reduction by addressing this component, and the use of alternative anodes or depolarisers such as methanol or hydrogen have been considered, as discussed under Anode Reactions earlier.

The electrochemical equivalent of zinc is 1.2195 g per ampere hour, or 820.0 ampere hours are theoretically required to deposit 1 kg of zinc. For a typical current efficiency of 92 per cent the actual charge required is 891.3 ampere hours per kg of zinc deposited.

Using the above cell voltage the energy consumption is $891.3 \times 3.395 = 3026$ DC watt hours per kg of zinc deposited. At 97.5 per cent efficiency of conversion of AC to DC power the electrolytic energy requirement is 3104 Wh per kg (or kWh per tonne). In practice energy consumption can range from 2900 to 3300 kWh per tonne.

The principal factors affecting energy consumption are the current efficiency and the solution potential drop. The factors influencing current efficiency are discussed in detail at the start of this chapter. Solution potential drop is a function of solution conductivity, and current density. If components of the cell voltage related to current flow are separated from the data given in Table 7.5 the approximate expression given in Equation 7.26 will apply.

$$\text{Cell voltage} = 2.67 + k_o \cdot (\text{Current density in amps/cm}^2) \quad (7.26)$$

The constant k_o may be further subdivided into three components (Kaneko *et al*, 1990):

$$k_o = k_1 + k_2 + k_3 \quad (\text{Typically } 15.2 \text{ ohm.cm}^2)$$

where:

$$k_1 = \frac{11 \cdot (\text{Electrode interface distance})}{(\text{Electrode conductivity})}$$

$$k_2 = \text{anode crust resistivity (typically } 2 \text{ to } 3 \text{ ohm.cm}^2)$$

$$k_3 = \text{other resistances such as contacts and electrode sheets (typically } 5 \text{ to } 7 \text{ ohm.cm}^2)$$

If the electrode interface distance is l cm then $k_1 = \frac{11 \cdot l}{K}$ where K is the solution conductivity as given

by Equation 7.25. Typical cell voltages may be calculated from equation 7.26 as expressed by Equation 7.27.

$$\text{Cell voltage} = 2.67 + j \cdot \left(\frac{11 \cdot l}{K} + 8.5 \right) \quad (7.27)$$

Because of the importance of the solution potential drop in determining energy consumption, attempts have been made to minimise the interface distance by more precise location of the electrodes. A system of holding frames has been introduced by Akita Zinc at its Iijima Smelter in Japan (Kaneko *et al*, 1990), whereby they were able to reduce the electrode pitch to 41 mm and the interface distance to 14.5 mm. Anode cleaning frequency had to be increased to a 48-hour cycle matching cathode stripping, which also reduced the anode crust resistance factor (k_2) from 1.9 to 0.1. As a result, energy consumption was reduced from 3301 kWh/t of zinc to 3041 kWh/t.

A lower current density will reduce voltage and will also reduce current efficiency. However, the effect of the voltage reduction on energy consumption is greater than the opposing impact of current efficiency within the usual operating range of 400 to 500 amps/m². Lower current density operations will require more cathode area or numbers of cells and associated equipment for the same zinc production. Hence there is a trade-off between cost of capital equipment and the cost of energy to arrive at a preferred current density. Often plants are initially constructed at modest current densities but marginally expanded by raising current density at the expense of electrical energy rather than additional capital.

Apart from these energy consumption issues, high current densities will increase the anode corrosion rate and the lead level in cathode zinc. This may impose some upper limits on practical current densities, but will depend very much on the particular electrolyte composition and the presence of corrosive elements such as chloride.

Solution composition affects conductivity, which is lower for high sulfate contents or high solution molarity. Hence the presence of unnecessary elements such as magnesium and manganese can raise cell voltage. High acidities will improve conductivity and reduce cell voltage, but will reduce the current efficiency at a constant zinc concentration as outlined earlier in this chapter. However, consideration of voltage effects will shift the optimum acidity to higher levels. Acidities can be raised without reducing

the zinc to acid ratio by also raising the zinc content and hence the zinc sulfate content of neutral purified solution. This will increase solution viscosity and reduce conductivity, and requires the other impurity elements such as magnesium and manganese to be minimised. However there are limits set by the solubility of zinc sulfate and the potential for associated double salts (such as zinc ammonium sulfate) to crystallise from solution at points in the circuit where the solution is at maximum concentration and minimum temperature – such as during the removal of gypsum from pure solution.

Increased temperature reduces conductivity and reduces cell voltage, but lowers current efficiency as discussed earlier. A compromise temperature is normally within the range of 36 to 42°C.

Anode scale contributes to cell voltage and attention to regular anode cleaning is important. Contact voltage drop can also be significant in a poorly maintained operation and contacts require constant attention in terms of cleaning and proper alignment and seating. Alignment also affects electrode spacing and, if misaligned, can impose considerable variation in current density at various positions across the surface of the cathode sheet. Contact potential drop is given as 24 mV in Table 7.5 as a typical value but can be as low as 15 mV and very much higher when the contact is badly corroded or poorly seated. Modern cell house designs provide for the collection of solution dripping from lifted cathodes to minimise spillage on contacts and bus bars, and also provide for contact washing to reduce corrosion. Infrared monitoring techniques are used for the detection of high voltage drop or ‘hot’ contacts.

Poor alignment of electrodes or bent electrodes can have a significant impact on average current efficiency through the resulting variability in current densities across the electrode surfaces. The practical impact of this on performance is often not fully appreciated.

Deposition Time

As indicated under Process Principles, current efficiency tends to decline at an accelerating pace with increasing ampere hours. This behaviour is very much influenced by the particular solution composition and trace impurity levels, but a typical set of data is shown in Figure 7.6 (Boissoneault, Robinson and Girard, 1998).

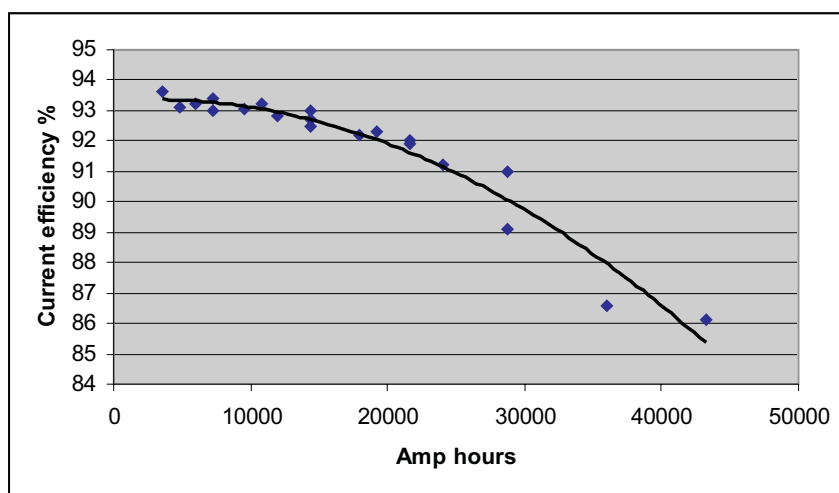


FIG 7.6 - Effect of deposition time (ampere hours) on current efficiency.

A general empirical rule from a range of operations suggests that:

$$\text{Optimum deposition time (hours)} = 120 - 0.14 \times \text{Current density in amps per m}^2.$$

Hence for 500 amps/m², optimum deposition time is 50 hours, close to the practical cycle of 48 hours, which is common practice. However with mechanised cathode stripping the trend is to strip as frequently as the machine and crane capacity will allow. This helps to maximise current efficiency, but increases the number of cathodes to be handled.

Cathode Deposit Purity

In general, many impurity elements will impact on current efficiency and must be removed for that reason. The resulting content of those impurities in the deposited zinc will then be so low as to have negligible effect on cathode deposit purity. This does not apply to cadmium and thallium. However cadmium is an indicator of efficient purification and if below a target level will ensure that other impurities, which can have an effect on current efficiency, have been efficiently separated to sufficiently low concentrations. At target cadmium levels of around 0.3 mg/L in purified solution the cadmium content of deposited zinc will be an order of magnitude below Special High Grade (SHG) specification levels in product zinc (0.003 per cent).

As indicated in Chapter 6, thallium must be below 1 mg/L to meet the 10 ppm limit in SHG zinc. This can normally be readily achieved if there is sufficient outlet for thallium from the solution circuit with iron in iron residues. However, conditions can occur when this is not achieved and thallium levels rise to the point where cathode zinc is out of specification. Usually this also corresponds with quite high levels of thallium in any product cadmium metal.

The level of copper in cathode zinc is generally well above the level that would correspond to the concentration of copper in purified solution. The additional source of copper is from the corrosion of bus bars and electrode contacts. This is minimised in a modern cell house by the collection of electrolyte dripping from lifted electrodes during transport on the overhead crane, and by the regular washing of contact bars with fresh water.

Lead is the major impurity in cathode zinc and must be below 30 ppm to meet the SHG specification. The source of lead is the corrosion of the anode, aggravated by high current densities and the presence of chlorides in the electrolyte. It is high with new anodes as detailed earlier in this chapter. The addition of strontium carbonate to the circulating electrolyte may be used to scavenge and reduce lead in cathode zinc as discussed in Chapter 6. Cathode zinc purity is monitored by regularly sampling by punching small discs at random from the stripped zinc sheets. The punchings are compounded into an analytical sample.

PLANT OPERATING AND DESIGN FEATURES

General

A generalised flow sheet for a modern zinc cell house is shown in Figure 7.7. Electrolyte is circulated through the cells and over a set of cooling towers before returning to the cells. Purified feed solution is added to the return electrolyte and an equivalent amount of spent electrolyte is taken from the exit flow and is directed to storage tanks prior to return to the leaching plant. Pure solution and spent electrolyte storage volume must be sufficient to cover any leaching-purification plant down-time and allow for continuous cell house operation at peak rates. Often the storage tanks may be interchangeable in duty between pure solution and spent electrolyte to optimise capacity requirements, since with a leaching plant shutdown pure solution storage reduces and spent electrolyte storage is maximised. However, at least one tank dedicated to each solution is required.

Manganese slimes from anode cleaning and cell cleaning are thickened, filtered and washed on a vacuum belt filter to recover entrained zinc sulfate. Manganese dioxide may be recycled to leaching for manganese balance control or may be disposed of if the input of manganese in zinc concentrate is sufficient to maintain minimum solution concentrations.

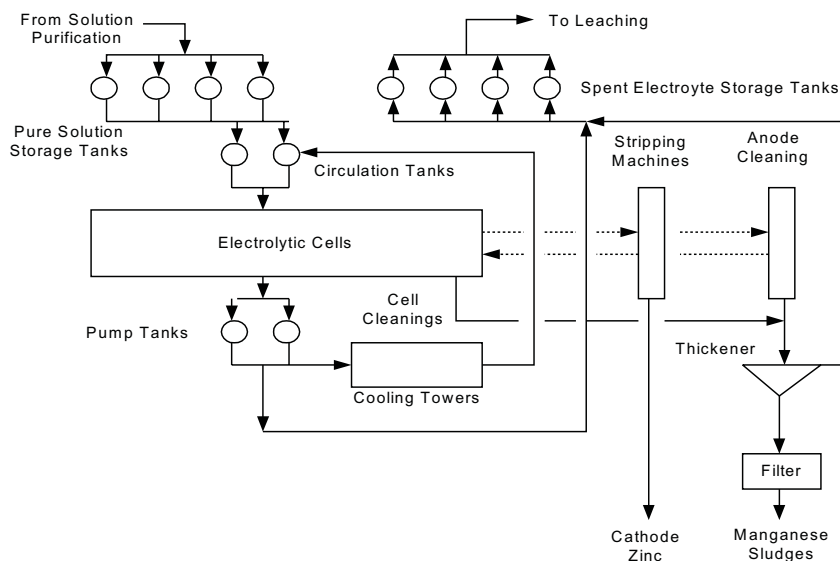


FIG 7.7 - Generalised cell-house flow sheet.

Electrolytic cell design is basically an open topped tank, into which are suspended alternatively closely spaced cathode and anode sheets (see Figure 7.8). This configuration provides the maximum possible deposition surface area for a given floor area.

The determining design feature is the size of the cathode, which in earlier plants was limited by the weight of the zinc sheet that could be manually stripped. The surface area was set at 1.0 to 1.2 square metres or 0.6 square metres per side and gave a zinc deposit of around 25 kg per side for practical current densities and deposition times. Dimensions of the cathode were approximately 600 mm wide and 1000 mm immersed depth. The greater depth to width aimed at minimising floor area.

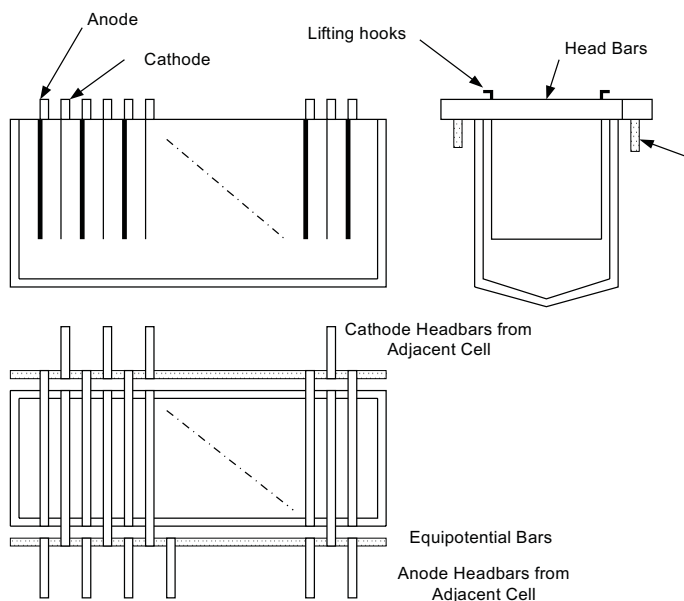


FIG 7.8 - Electrolytic cell construction and layout.

Cells are designed with a cross section substantially deeper than the electrodes to allow for the collection and accumulation of sludges, in particular MnO_2 , which is periodically removed by suction hose or by draining through a bottom valve in the cell.

Older plants had around 40 cathodes (and 41 anodes) per cell, but with improved DC electric power supply allowing for increased currents, with improved construction methods to achieve precise tank levels, and with increased crane capacity, the cell size has been increased to over 120 cathodes per cell (Tamargo and Lefevre, 1993; Caufriez, Dubois and Lejay, 1998; and Lefevre and Pieterse, 1998).

With the development of mechanical stripping machines and automated electrode handling, it has also been possible to increase the size of the cathode. This resulted in the introduction of the 2.6 m² 'Jumbo' cathodes in 1969 followed by the 3.2 m² 'Super Jumbo' cathodes in 1979. Subsequent cell house designs have not increased cathode areas significantly, since the limit of the capacity of the resting electrical contact to carry heavy currents has been reached. Various types of resting contact designs have been developed but it would appear that given these constraints, the present cathode size is limited to around 3.4 m². (1 m wide by 1.7 m immersed). For normal operating current densities of around 450 amps/m² this corresponds with a total supply current per cathode of around 1500 amps. Considering that half the cathodes are lifted out of the cell for stripping, the remaining cathodes during that short period of removal and before replacement of fresh cathodes, will carry twice the normal current or 3000 amps per contact. However this is only for a short period and should not result in excessive heating of the contact. Voltage drop across the contact is an important control parameter and should be in the range of 10 to 15 mV per contact in normal operation. Clamped contacts could remove this limitation but would need to accommodate the smooth and simple lifting of cathodes for stripping.

The other issue with large electrodes is the current carrying capacity of the electrode plate, which will require increased thickness to adequately distribute the current over the plate area. Also there is a need for planar stability and avoidance of bending or warping, which can cause large local variations in current density and hence cause significant loss of current efficiency. In the extreme, it can also cause short-circuiting by contact with an adjacent electrode. Planar stability becomes more difficult as the size increases and, to compensate, some increase in the electrode spacing is allowed. However, this increases cell voltage, in turn increasing the cost of electric power. All these factors lead to an optimisation of electrode size, which with present technology is in the range of 3.2 to 3.4 m² per cathode.

Electrode spacing varies from one plant to another but must allow for the thickness of the electrodes and for the growth of the deposit without touching and short circuiting. Allowance is also made for the anode crust, for distortions of the electrode plates, and for some misalignment. A practical interface distance is between 30 and 40 mm, and for large electrodes gives a pitch between the centre line of adjacent cathodes (or anodes) of around 90 mm.

To prevent adjacent electrodes from touching, it is common to place insulator 'buttons' on the surface of the anode to act as spacers. They are usually fabricated from polypropylene as a conical projection attached as a nut and bolt through a hole in the anode sheet. A number of these insulators may be distributed over the face of the anode. Usually they cast a shadow in the electric field and the cathode zinc deposit opposite their position is much thinner. Care is needed in the design of the insulator profile to avoid damage from the cathode sheets as they are lifted from the cell and returned.

In original plant designs, cells were separate and fed power through individual copper bus bars. This arrangement incurred considerable cost in bus bars, corresponding power losses and was wasteful of floor area. Later designs placed cells together with the anodes of one cell connected to the cathodes of the adjacent cell via an equipotential bar placed between the edges of adjacent cells, as shown in Figure 7.8. A series electrical connection is built-up in this way to a maximum overall voltage of 500 VDC to give the modern cell layout as shown in Figure 7.9.

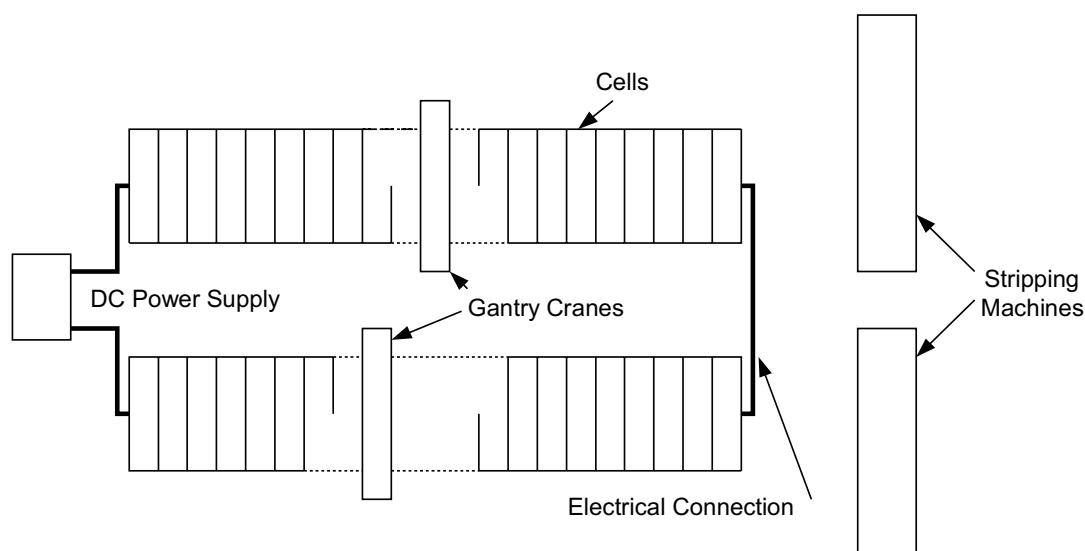


FIG 7.9 - Electrolytic cells layout for a modern tankhouse.

The configuration of cells is often as two parallel rows, electrically arranged as a U so that the power connection can be at one end, thus limiting the length of the supply bus bars from the rectifier – transformer. This is particularly important as the size of the electrodes and cells, and hence the supply current is increased.

Cells are commonly constructed of polymer concrete and lined with PVC liners. The cells may be individual tanks or in some designs are based on inverted T sections butted together and lined with flexible ‘Paraliners’ (Tamargo and Lefevre, 1993).

Removal of electrodes from the cells is by means of overhead gantry crane straddling each cell row. In the past, various crane designs have been used, from individual hoists mounted on crawl beams to multi-use cranes feeding onto a transfer conveyor, which in turn feeds the stripping machines.

The number of electrodes in each cell is largely dictated by the span and lifting capacity of the electrode handling crane. It is normal practice to lift every second cathode for stripping, which allows for the minimum number of crane movements. Older plants had reduced lifting capabilities and more frequent movements. Current designs can allow up to 130 cathodes per cell, which requires a crane span of about 12 m, capable of lifting up to 65 cathodes and up to 15 tonne. The other important feature is the speed of the crane movement in enabling the transfer of cathodes to the stripping station and return of fresh cathodes to the cell. The improvements in high speed automated crane operation has considerably extended the scope of cell unit design and has reduced the capital cost of electrolytic plants.

The electric supply limitation, set at less than 500 VDC, determines the number of cells in a unit and is purely a safety consideration for operations where there is exposure to wet conditions and conductive solution. There is general reluctance to raise unit electrical supply voltages further for these reasons, and clearly if this was applied, much more extensive electrical isolation would be necessary.

Characteristics of typical older style and new generation cell houses are given in Table 7.6. Also shown are the average and extreme characteristics from a world survey of electrolytic zinc plants (James, Waters and Peter, 2000).

TABLE 7.6
Cell house characteristics.

Parameter	Typical Older Style	Typical Modern	World Average	World Maximum	World Minimum
Spent electrolyte					
Zn g/L	50	50	60	70	47
H ₂ SO ₄ g/L	165	165	164	200	135
Current density(amps/m ²)	500	450	510	640	281
Cathode area m ²	1.2 - 1.7	3.2 - 3.4	2.1	3.4	1.0
Electrode spacing mm	75	90			
Cell temp °C	38 -40	37			
Current efficiency %	90	93	90.3	93	87.3
Cathodes per cell	40	100 - 120	48	112	18
Cell voltage	3.5	3.3	3.44	3.75	3.1
Deposition time (hrs)	48	48	35	72	16
Energy use (kWh/t)	3300	3000	3202	3477	2970
Ag content of anodes	0.5 - 0.75%	0.5%			

Cathodes, Cathode Stripping and Handling

Cathode stripping was originally a manual operation but this involves heavy labour and the high risk of back injuries. Consequently, most plants have converted or are fully designed for mechanised stripping. There are many proprietary mechanical stripping systems, but most operate on the principle of a parting knife which is forced between the zinc deposit and the aluminium cathode sheet. Once detachment occurs, the zinc sheet is peeled from the aluminium using an extended blade. The means of entry of the parting knife is the subject of many patented procedures. Most use some form of plastic insert or attachment to the cathode sheet (such as an insert disc or a swing flap), which provides an area free of zinc deposit and an overhanging edge, under which the parting knife can secure access and prise the zinc deposit away.

It is also important that the cathode sheet is fitted with edge strips to prevent zinc growth around the edges linking the deposits on each side and preventing separate detachment. The design of the edge strip attachments is of considerable importance. They must be robust and able to withstand the forces associated with stripping, and can be a source of significant problems when they become detached during handling and stripping.

Dendritic growth of zinc over and around the edge strips can occur, and must be removed as it can grow and cause electrical shorting between the cathode and anode. This may require periodic manual intervention in the stripping operation for inspection and removal of such deposits.

Periodic brushing of the cathode sheets is practiced during the stripping operation to buff the surface and remove any minor dendritic growth as well as promoting the formation of an aluminium oxide film that improves the ease of stripping, and as some may claim, improves the morphology or smoothness of the zinc deposit. Brushing may be practised every time the cathode is stripped, but more commonly is every second or third occasion. Cathode sheets with excessive unstripped and strongly adhering zinc deposits are removed from the system and are pickled in spent electrolyte to dissolve off the adherent zinc. A feature of mechanical stripping machines is a facility for weighing stripped sheets and rejecting those that exceed the nominal 'clean' weight. Rejected cathodes may then require pickling. In addition, pickling may be conducted on a regular basis.

The life of cathodes is typically around five years and often a partial replacement is made by cutting the sheet from the headbar just above the 'waterline' and welding on a replacement, thus allowing the headbar assembly to be used a second time.

The speed of a mechanical stripping machine is of importance in determining the number of machines required for a given production capacity. A common standard is of the order of ten seconds per cathode sheet, although this is likely to be longer for larger cathodes and shorter for smaller cathodes where less than five seconds is possible. Machine times should also allow significant time for maintenance and often stripping is planned for less than 16 hours per day with the remainder allowed for maintenance and other activities such as anode cleaning.

Another optional feature on stripping machines is the facility to wash cathodes prior to stripping. This removes adherent salts and residual sulfuric acid, and reduces the amount of dross formed during subsequent melting. It also provides some reduction in potential corrosion of the stripping and handling equipment. The degree of reduction in dross formation varies considerably with the physical nature of the zinc deposit, but can be of the order of 0.5 per cent of the cathode zinc production.

The design of the stripping machine must be integrated with the performance of the crane used for lifting cathodes, and should be able to match the cycle time for lifting and transport of cathodes from the furthest cell. In this regard, high speed automated cranes are an important feature of a modern cell house. The total crane cycle involves the following actions:

- lifting cathodes from the cells;
- transporting the lift to the stripping station;
- depositing the cathodes in the stripping machine input conveyor;
- moving to, and locating a set of stripped cathodes in the stripping machine output conveyor;
- transporting the stripped cathodes back to the cell;
- locating in the correct position above the cell and depositing the cathodes;
- locating the next lift of cathodes in the same cell or moving to the next cell and locating the correct position for lifting cathodes; and
- repeating the cycle.

In some plants, a number of cranes are used to feed a conveyor system feeding the stripping machine. However modern systems tend to closely match large automated and high speed gantry cranes with stripping machines. A typical layout for an integrated arrangement is given in Figure 7.9.

Anodes

As indicated under Anode Reactions earlier in this chapter, anodes are usually made of lead containing at least 0.5 per cent silver. For large sized anodes, dimensional stability becomes important and this can be achieved by increasing the thickness. However, this significantly increases the weight and the associated problems of support and of routine lifting for cleaning. Perforated sheets may be used to reduce weight. Alternatively, ribbed sheets providing rigidity with minimum weight have been applied, but the use of rolled sheet rather than cast plates is becoming more common. The use of calcium as an alloying component also has benefits, since it results in a harder material with a higher tensile strength, thus allowing for reduced thickness and weight. Standard rolled anodes of 3.2 m² area are of the order of 10 mm thick and have a weight of around 400 kg. The total load of anodes in a cell containing 100 cathodes and 101 anodes would be around 40 tonne, which requires substantial support structures. The removal of anodes will also tend to dictate the lifting capacity of the crane – although it may tend to operate at reduced speed when processing anodes.

There is evidence to suggest that calcium alloys result in reduced corrosion and more efficient removal of scale. Silver levels can be reduced marginally if calcium alloys are used.

New anodes are pretreated, as indicated under Anode Reactions, to form a PbO₂/MnO₂ layer and minimise initial corrosion rates. It has also been found that sandblasting of new anodes modifies the

surface grain structure so as to enhance the formation of PbO_2 and so reduce the required conditioning time (Prengaman and Siegmund, 2000).

Anode life has traditionally been of the order of five years but Asturiana de Zinc have reported life of eight years for their cell designs with the use of rolled calcium alloys (Lefevre and Pieterse, 1998).

Electrolyte Flow Control and Composition

Electrolyte is generally circulated through each cell so as to maintain a constant composition with respect to zinc and acid concentrations. Electrolyte exiting the cells is pumped to a cooling tower. A bleed of spent electrolyte passes to storage tanks for return to the leaching operation, whereas the bulk is mixed with fresh incoming feed solution and is returned to the cells. The circulating flow may be 15 to 20 times the net feed solution flow.

Most plants operate with a purified solution concentration in the range of 150 to 180 g/L zinc entering the cell house, and operate with a spent electrolyte composition of around 50 g/L zinc and 165 g/L sulfuric acid. As indicated under Process Principles, the zinc to acid ratio is an important determinant of current efficiency, empirically expressed by Wark's Rule (Equation 7.17). High current efficiency is favoured by a high zinc to acid ratio. As opposed to this, the volume of circulating solution to be handled through the leaching and purification operations is determined by the reduction in concentration of zinc during electrolysis. The greater reduction per pass, the lower the zinc to acid ratio, hence the lower will be the volume of solution circulated and the corresponding size of the leaching and purification plant. There is thus a compromise between the current efficiency and the circulating volume as illustrated in Table 7.7, based on a pure solution strength of 150 g/L Zn and a Wark's Rule constant of 30.

TABLE 7.7
Current efficiency and circulating volume relationship.

Spent electrolyte - Zn g/L	100	85	72	58	45	32
Spent electrolyte - H_2SO_4 g/L	100	120	140	160	180	200
Relative volume circulated	1.00	0.81	0.70	0.61	0.54	0.49
Current efficiency %	96.8%	95.5%	93.8%	91.5%	88.2%	82.7%

The compromise position is taken at a current efficiency of marginally above 90 per cent to give the selected spent electrolyte composition at around 165 g/L acid strength and 50 g/L zinc. This is a simplification and there are other issues involved. It will also vary from plant to plant depending on economics and equipment available. Actual current efficiency relationships will also depend on the particular suite of impurities present and the degree of purity of the electrolyte as covered under Process Principles.

If it is desired to raise the acidity in all or part of the spent electrolyte, such as for use in strong acid leaching, then a separate series of cells may be used. These cells operate as a separate circuit with normal spent as the feed, and limits the sacrifice of current efficiency to only those cells. This arrangement can optimise overall performance, and the second set of cells is termed a 'Spent Stripping' circuit. The optimisation of current efficiency may be illustrated by using the data of Table 7.7 for a fixed final acidity of 200 g/L and is shown in Table 7.8.

The optimum on this basis would be for Circuit 1 to operate with a spent acidity of 140 g/L, depositing 70 per cent of the zinc production, and the Spent Stripping circuit (2) raising the spent acidity to 200 g/L and depositing 30 per cent of the zinc production. This serves to simply illustrate that current efficiency may be optimised by splitting the solution circuit into two series arrangements. In practice spent electrolyte acidity is often raised only for that portion used for ferrite leaching, which may

TABLE 7.8*Optimisation of current efficiency using spent stripping.*

Circuit 1 Spent acidity g/L	100	120	140	160	180	200
% of total zinc deposited	50	60	70	80	90	100
Circuit 1 Current Efficiency	96.8%	95.5%	93.1%	91.5%	88.2%	82.7%
Circuit 2 Spent acidity g/L	200	200	200	200	200	
% of total zinc deposited	50	40	30	20	10	0
Circuit 2 Current Efficiency	82.7%	82.7%	82.7%	82.7%	82.7%	
Overall Current Efficiency	89.6%	90.4%	90.5%	89.8%	87.7%	82.7%

represent less than half of the total flow. The spent stripping circuit in that case would represent a much smaller proportion of the total zinc production – less than 15 per cent on the above basis and, practically, is likely to be less than ten per cent.

Consideration of issues related to cell voltage and overall electrical energy consumption will shift the optimum to higher acidities than this simple illustration might indicate.

As indicated in Cathode Reactions ‘Cathode Deposit Morphology’ (the overall solution molarity, or total salt content) is also an important issue. If too high, it will excessively raise cell voltage and will aggravate the formation of nodular cathode deposits. High molarity can often arise where high levels of magnesium are present in solution.

Heat Removal

The electrical energy used is expended either as chemical energy, which is equivalent to the reversible cell potential, or as heat. Heat represents close to 40 per cent of the electrical energy input and for the deposition of 95 g/L of zinc from pure solution at an electrical input of 3.1 kWh per kg of zinc deposited, heat generation is 1.2 kWh per kg of zinc or close to 118 Wh per litre of solution. This is sufficient to raise the temperature of the solution by 98°C. The high level of circulation of electrolyte at about 20:1 will reduce this to about 5°C as the expected temperature rise per pass of solution through the cells.

Evaporative cooling towers are used to remove the heat and drop circulating electrolyte temperature to about 5°C below the desired operating cell temperature. The evaporation achieved in the cooling towers is of the order of ten to 15 per cent of the incoming feed solution volume, but is dependent on ambient conditions.

Older cell designs used cooling coils inserted into the cells and did not operate with a circulating electrolyte system. In this case, fresh feed solution is added individually to each cell to maintain the required spent electrolyte acidity. Control is required on each cell and is far more difficult to maintain than with full high volume solution circulation. Also, with cooling coils there is minimal evaporation leading to difficulties in the control of water balance in a closed electrolyte system.

Cooling towers are generally unpacked spray towers fitted with large fans for countercurrent air flow. Efficient mist eliminators are needed at the top of the towers to prevent physical loss of electrolyte. Due to the evaporation and temperature change, gypsum will deposit on the walls of the towers and provision needs to be made for cleaning at regular intervals. The amount of gypsum deposited can be considerably reduced by the use of a separate evaporative cooling system or gypsum removal system on pure solution prior to entering the electrolytic circuit. By cooling this solution to a relatively low level of 25°C in the presence of gypsum seed particles, gypsum will be removed, lowering the concentration in electrolyte to below saturation at the normal operating temperature and minimising fouling of the cooling towers as well as the total electrolytic circuit. This is covered in Removal of Gypsum in Chapter 6.

The desired operating temperature of electrolytic cells is a compromise between a number of opposing effects, in particular cell voltage (hence energy consumption) and current efficiency. In addition, higher temperatures will increase the corrosion of the lead anode and raise the level of lead in cathode zinc. As detailed under Electrolyte Conductivity and Zinc Cell Performance in this chapter, the optimum operating temperature is generally in the range of 36 to 42°C. The generation of acid mist is aggravated by raising the electrolyte temperature and is often a reason for limiting cell temperature.

Acid Mist

Mist is formed at the surface of the cell by the collapse of gas bubbles (oxygen and hydrogen). The size of the droplets of electrolyte formed is a function of the solution surface tension and viscosity. Fine droplets will form a mist of the acidic electrolyte, which is an irritant to the respiratory system and has been classified as a low level carcinogen. Suppression of acid mist is therefore of considerable importance. This is usually achieved by the addition of organic reagents, which modify surface tension and form a foam blanket on the surface of the electrolyte in the cells. There are a number of proprietary materials available but it is important that the effects on a particular electrolyte, such as the impact on current efficiency, are adequately tested. Mist formation differs widely at different plants, some indeed can avoid the use of additives altogether.

Apart from mist suppression, adequate ventilation is most important for operator comfort and protection. Many different ventilation systems are incorporated into modern cell house designs, but cross flow over the top of the cells would seem to be the most effective approach. The integration of ventilation with air intake to the electrolyte cooling towers is also a feature of modern plant design and allows for the capture of any acid mist without fugitive emission to the atmosphere.

Anode Management and Anode Slime

Anode maintenance and cell cleaning is an important aspect of cell house operation. Anodes need to be regularly removed and cleaned by scrubbing off the manganese dioxide deposit. Cleaning is generally mechanised and automated. Anode cleaning machines use brushing and high pressure water jet cleaning to dislodge the scale. However, it is important to take care in scale removal to avoid severe scrubbing and expose fresh lead metal surfaces. Exposed surfaces will result in high lead corrosion rates before a new scale coating is established, leading to high levels of lead in cathode zinc. Behaviour then reverts to that of a new anode as mentioned in the section on Anode Reactions.

The frequency of anode cleaning can be from twice per month to once every three months depending on the level of manganese in solution. The other important feature of anode cleaning is to ensure that the anodes are straight and flat before they are returned to the cells, and a mechanical device for this purpose is usually included within the anode cleaning machine.

Anode slime – principally manganese dioxide with high levels of lead sulfate and strontium sulfate, (if strontium carbonate is used for lead control) – forms in the bottom of the cells and must be periodically removed. This is usually done by either draining from beneath the cells or by pumping out from the surface. In the latter case, the cell needs to be taken out of service by electrical isolation, usually done by placement of shorting bus bars spanning adjacent equipotential bars. Cleaning frequency can range from monthly to annually depending largely on the manganese loadings and the holding capacity of the cells.

Anode slime can be difficult to handle in terms of settling and filtration properties, and these difficulties can be aggravated by excessive agitation and pumping, which tends to break-up the structure of the material into very fine particles. From this viewpoint, drainage from the cells directly to a washing filter with minimal disturbance is the preferred approach.

In general, lack of attention to anode condition is often a cause of poor cell house performance in terms of both current efficiency and zinc deposit quality. A golden rule for cell house operation is the maintenance of electrodes in a 'clean and straight' condition.

Electrolytic Solution Quality Monitoring

Normal solution quality control is by detailed analysis of key elements in purified solution as discussed in Chapter 6. Performance limits for good current efficiency will vary from one plant to another depending on the particular mix of impurity elements and additives used, but the important issue is to control consistency in the quality of solution. Regular on-line analysis of all impurities is generally not required and it is usually sufficient to monitor only copper, cadmium and cobalt continuously as a basis for solution quality control. Continuous monitoring of spent electrolyte acidity is an important control and usually is measured using electrodeless conductivity probes. Continuous in line analysis of the zinc content of spent electrolyte is also a key control measure and these two measures can be used for automated control of spent electrolyte off-take and feed solution addition.

Various overall feed solution quality measurements have been devised based on electrochemical measurement of solution characteristics. These usually rely on the measurement of cathode potential for electrolytic deposition of zinc on a fresh aluminium surface. Additives such as glue and potassium antimonial tartrate can be controlled and optimised by such devices. Usually results from one plant cannot be related to another and such measurement techniques are purely empirical indicators.

Another useful device is the Hull Cell, which employs a cathode plate inclined to the anode giving a variable gap and hence a variable current density. The critical current density at which zinc commences to deposit and above which a smooth deposit is obtained, can be measured and used for additive optimisation. However it is reported that these measurements are not particularly reproducible or reliable. The Hull Cell demonstrates critical current densities for the onset of zinc deposition ranging from 30 to 80 amps/m² (Hosny, O'Keefe and James, 1989).

Current Modulation

Where there is a high differential between the cost of peak and off-peak electric power, some plants will modulate power input to the cell house, operating at normal levels during off-peak and reducing to minimum currents during peak times. The minimum current densities used are generally around 70 amps/m² and will result in a current efficiency for deposition in the range of 50 to 70 per cent. This is essentially a holding operation with some deposition, but avoiding re-solution of the zinc deposit, which would occur if the current is reduced too far. This practice will mean that the cell house must be considerably larger than if operating at full power at all times. There must be a balance between the cost of peak load power and the capital cost of the additional cells and power supply equipment.

Zinc deposited on a fresh aluminium cathode sheet at low current density has a tendency to stick and be difficult to strip. Consequently a minimum of 150 to 200 amps/m² is used when fresh cathodes are in place. After initial deposition, current density can be reduced back to minimum levels as above. This form of current modulation has been common practice in Japan and Korea.

Periodic interrupted current supply, or even current reversal, has been used in Russian and Bulgarian plants. This is reported to reduce concentration polarisation or overvoltage, reducing average cell voltage and hence energy consumption. It also improves the structure of the deposit and allows for longer deposition times. The complications of electrical supply switching and the reduced plant capacity will however negate any minor advantages from this practice and it has not been followed elsewhere.

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Melting and Casting

PURPOSE

The purpose of the melting, alloying and casting operations as part of an electrolytic zinc plant is to convert cathode zinc into marketable product metal. Zinc metal may be marketed as pure metal or as alloys, and is delivered in a variety of ingot shapes ranging from around 10 kg to 1000 kg or greater.

The operations consist of cathode melting, alloy preparation, ingot casting, product preparation, such as forming ingot bundles, and product dispatch. An important part of these operations is product quality control.

A schematic of the operations involved is shown in Figure 8.1.

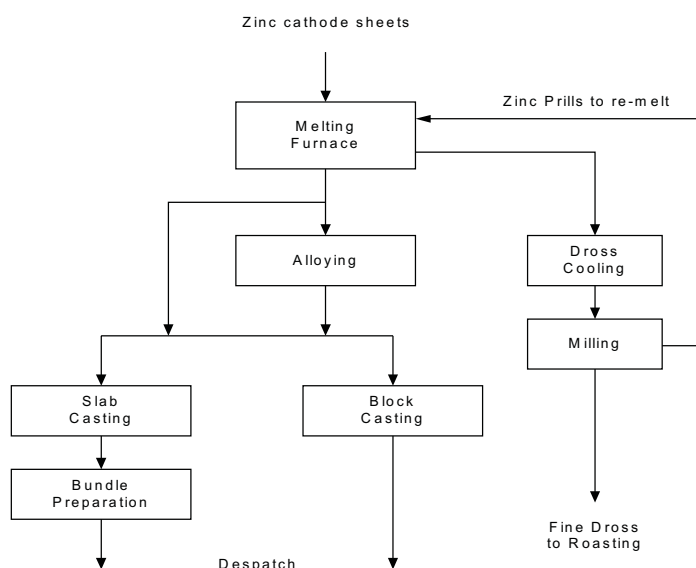


FIG 8.1 - Melting and casting operations.

CATHODE MELTING

Although gas or oil fired reverberatory furnaces were used in the past for cathode melting, low frequency electric induction furnaces of a relatively standard design are now almost universally used. The most common design is the Ajax Magnathermic design consisting of a 30 to 45 tonne capacity brick lined furnace fitted with four channel type, mains frequency inductors, two on each side of the furnace as illustrated in Figure 8.2.

Inductors use the principle of the transformer, with a loop of molten metal forming a short circuited secondary winding. Design for zinc melting is based on the use of three channels per inductor to produce a circulation or pumping action of the molten zinc, which enters through a central channel and exits through the two side channels. Inductors are lined with a rammed refractory and the technique for ramming and curing the refractory is particularly sensitive, but, if done well, can see a life of more than ten or 15 years before replacement is necessary. The primary coils are usually air-cooled and have various tappings to allow control of the power input.

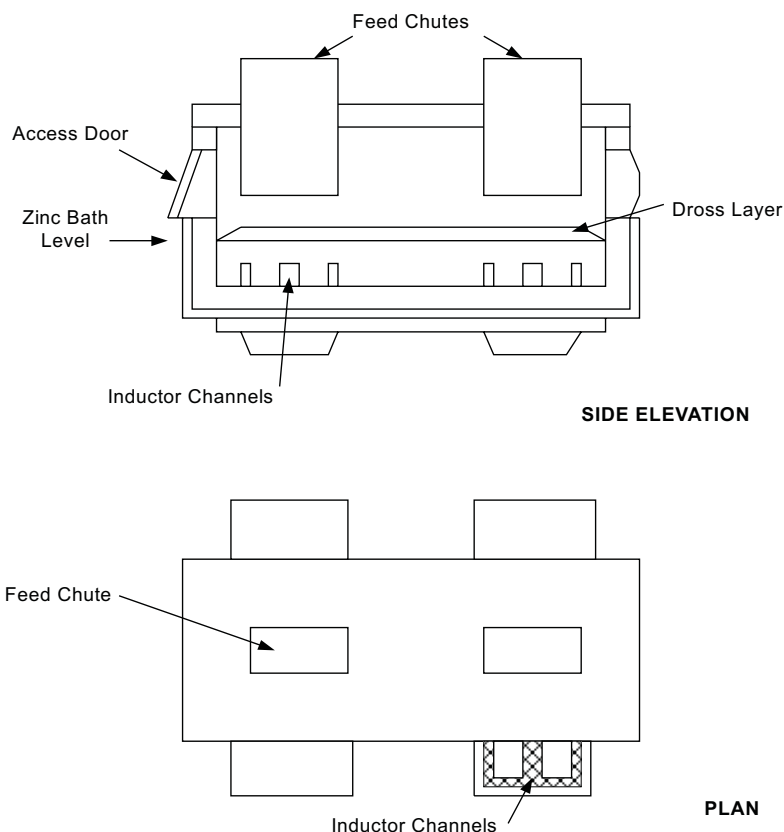


FIG 8.2 - Schematic of an electric induction melting furnace.

Cathodes are fed into the furnace through one or two vertical chutes located centrally between two inductors. Molten zinc circulates through the inductor channels and impinges on the cathode sheets, promoting rapid melting. Cathode feeding is usually from a platform or floor above the furnace. Bundles of washed cathodes are placed on a tilting table that lifts and discharges the sheets down the feed chute. It is important to keep the chute full and avoid damage to the furnace floor by falling zinc sheets. A hinged and hydraulically operated arrestor plate can be fitted to the chute to control the flow of sheets into the furnace and this may be automatically controlled by the level of molten zinc in the furnace. Keeping the chute full also preheats and dries the cathodes, ensuring that only dry material enters the bath. This reduces oxidation of the zinc and avoids the risk of explosions.

Melting temperature is controlled at around 500 to 520°C and is limited to minimise volatilisation and oxidation of the zinc. Inductor power ratings can be up to 450 kW each and with four inductors of this size, a furnace is capable of melting about 18 tonne per hour of cathode zinc. Heat required for melting to 500°C is 88 kWh/t and furnace losses are of the order of 250 kW, giving an overall energy consumption of around 103 kWh/t. For smaller furnaces this may rise to 120 kWh/t.

Fluxing and Dross Handling

Zinc oxide forms during melting due to direct oxidation of the zinc surface and due to the decomposition of zinc sulfate entrained on the surface of the cathode by reaction with molten zinc according to Equation 8.1.



Drainage and washing of the cathodes during stripping to remove electrolyte salts is important in reducing dross make. The oxide and residual salts float to the surface of the melt, forming a dross layer, which contains a high proportion of occluded zinc droplets. To reduce the occlusion of zinc, ammonium chloride is added as a flux through the feed chute with the zinc cathodes. The ammonium chloride sublimes and decomposes at the melt temperature forming NH_3 and HCl gases. The HCl readily reacts with zinc oxide to form zinc chloride with a melting point of 322°C . A eutectic between ZnSO_4 and ZnCl_2 , and also $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$, form molten phases, which in effect liquefy the oxides and salts coating zinc droplets, allowing them to coalesce, and thus facilitating the drainage and separation of zinc from the oxide dross. Excessive use of ammonium chloride will result in a high level of fume generation from the melting furnace. This tends to deposit on colder sections of the ventilation ducts, eventually causing blockages. This in turn reduces the effectiveness of furnace ventilation and causes excessive fume emission into the working environment. Normal additions of ammonium chloride to the melting furnace are of the order of 0.5 kg/tonne of cathodes melted.

Dross is allowed to build up as a blanket layer on the surface of the molten zinc to restrict oxidation, but must be periodically removed. This is done by manual raking across the surface into a chute or transport hopper located at the furnace access door. This operation generates a lot of fume and adequate ventilation must be provided. Automated mechanical dross removal is not common, but is desirable to reduce air inflow to the furnace. Furnaces blanketed with nitrogen are used and substantially reduce dross formation, but at a significant additional operating cost.

Dross formation from the melting furnace may be three to five per cent of the mass of cathodes melted, but part of this is recovered as metallic zinc for re-melting and the net loss of zinc as fine oxide dross from the melting furnace is of the order of 2.5 per cent with a range from one per cent to 3.5 per cent. Dross production from reverberatory melting furnaces is much higher at between 3.5 and five per cent net, after recovery of metallics. These furnaces also impose a much larger ventilation load.

Dross processing methods vary, but usually involve cooling followed by milling in an air swept rotary mill to separate fine oxides from metallic zinc prills. The zinc prills can be re-melted and the fine oxides carried from the mill in the air stream are captured in a bag filter. Ventilation gases from the furnace are also passed through a bag filter to capture the fume. This is normally combined with fine dross and is fed to the roasting plant to remove chloride prior to recycle to the leaching plant. The total quantity of dross and fume recycled to the roaster represents around 2.5 per cent of cathode zinc with a range of one to 3.5 per cent.

Other methods of dross processing include hot drossing drums where more ammonium chloride is added to allow molten zinc to drain, as well as screening, with the return of coarse sized material for re-melting and fines recycled to the roasting plant.

Molten Zinc Transfer

Molten zinc is normally pumped from the melting furnace using submerged centrifugal pumps fitted into a side pump well. Pumps are usually constructed from silicon carbide for the body and impregnated graphite for the impeller. The molten metal discharges from the pump line into an open launder system for distribution to alloying or casting facilities. Launderers can be refractory lined steel channels, which can be heated indirectly or with a gas flame. Normally V shaped channels are used, lined with a refractory cloth impregnated and surfaced with fireclay. A launder slope of the order of one in 100 is sufficient for flow of molten zinc without excessive turbulence.

SPECIFICATIONS AND ALLOYING

More than half the zinc produced is, on average, simply sold as the unalloyed base metal in three grades:

1. Prime Western Grade – PWG (or Good Ordinary Brand – GOB).

2. High Grade - HG.
3. Special High Grade - SHG.

The reasons for these grades are historical, determined by the levels of impurities that could be readily achieved by the technology of the day. Electrolytic plants achieve SHG specification and most base zinc metal is traded as a commodity in accordance with this quality. This grade also forms the basis of most alloy production.

Specifications for impurity contents are given by various Standards such as ASTM B6-87, BS 3436:1986, and DIN 1706-1974. The London Metal Exchange (LME) also specifies minimum purity for zinc metal constituting 'good delivery' under their contract rules. Specifications are detailed in Table 8.1.

TABLE 8.1
Standard zinc quality specifications.

Grade	SHG	HG	PWG
Max Lead content	0.003%	0.07%	1.6%
Max Cadmium content	0.003%	0.03%	0.5%
Max Tin content	0.001%		
Max Iron content	0.003%	0.02%	0.05%
Max total impurities	0.01%	0.1%	2.0%
LME min zinc content	99.995%	99.95%	98.0%

A wide variety of alloys are produced for applications such as continuous steel sheet galvanising, diecasting, rolled sheet production and dry cell batteries. The usual alloying elements are aluminium, magnesium, copper, and nickel. In some cases, such as for dry cell battery alloys, cadmium and lead may be added and for continuous galvanising alloys (Galfan), aluminium and rare earth metals (Mischmetal) can be added.

Batch mixing is the common alloying procedure, using a ladle equipped with mixer and supported on load cells. Tilting coreless induction furnaces or gas fired alloying furnaces can also be used where heat addition is required. Alloy may be cast directly from the ladle or the tilting induction furnace, or via a larger holding furnace if production quantities are large.

Alloying components are batch weighed and mixed thoroughly to ensure dissolution prior to casting. Mixing times depend on the rate of dissolution of the components in molten zinc if added in solid form. In some cases, such as the addition of nickel, the rate of dissolution can be very slow and it is necessary to add the components in a finely divided or powdered form.

Otherwise, addition as granules is common to facilitate handling and weighing and enhance the rate of dissolution. Where large additions are made, as is often the case with aluminium, it is also common to make the addition in molten form. In that case mixing and dissolution is far more rapid. Master alloys in zinc can also be used for components that are difficult to melt and dissolve, such as mischmetal and also nickel.

Continuous alloying by mixing weighed streams of components into a controlled flow of molten zinc has significant advantages. If the additions are small, feeding as wire is possible; otherwise granule or powder addition using weighfeeders is used. The advantages of this system are the maintenance of a higher consistency in composition in comparison with batch systems and a minimum inventory of metal prior to casting, with greater flexibility in accommodating alloy changes.

If a holding furnace is used for alloy prior to casting, there can be issues in relation to the changeover from one alloy to another and the avoidance of cross contamination. This generally results in some level of rejection and recycling. The ability to fully empty the holding furnace avoids this problem and favours the use of tilting gas fired ladle furnaces or tilting coreless induction furnaces for this duty, rather than the channel type induction furnace, which must retain a minimum level of molten metal.

CASTING

There are broadly two types of ingot produced:

- slabs that can be manually handled – generally between ten and 25 kg; and
- blocks, which are generally of the order of 1000 to 2000 kg and are produced in a wide variety of shapes to suite customer requirements.

Slab Casting

Two general types of machine are used for slab casting – the rotary wheel caster and the straight line chain mould machine.

The casting wheel uses a rotary table with water-cooled moulds arranged around the outer periphery of the wheel. Molten metal is poured into the moulds at a fixed station. The mould then moves around with the wheel until close to the return position when the mould is rotated through 180 degrees and the slab released onto a collection conveyor. The mould is then returned to its upright position ready for refilling. These machines were the first of the mechanised casting lines and have largely been superseded. They are not highly productive for their size and the relatively large floor area occupied.

The straight line machines use the principle of a continuous line of moulds attached to two parallel chains driven by a variable speed tractor or caterpillar type drive. The line is inclined upwards from the pouring end and passes through a hood where water sprays are applied. Zinc slabs are released as the chain turns over at the upper end to return. At the lower end zinc is poured into the moulds at a controlled rate usually set by the speed of the pump in the relevant supply furnace. The machine speed can also be set and adjusted to give the required production rate.

There are many different pouring devices aimed at interrupting the flow of molten zinc between one mould filling and the next arriving at the filling position. These devices are in the form of wheels and tilting (or oscillating) ladles. Their performance is largely judged by trouble-free operation and by the amount of dross generated. To minimise dross formation, gentle flow of metal into the mould is essential, without generating turbulence or air entrapment, such as would occur by pouring from a significant height above the mould. Following the pouring position, there is a skimming station where dross is skimmed from the surface of the ingot. Complete removal of dross is important for the production of high quality slabs and to avoid mechanical interference with the operation of automated bundle preparation equipment. Many automated skimming devices have been designed, but few have been able to perform with complete satisfaction and this commonly remains a manual task in most plants. Improved robotics technology mimicking manual operations has the promise of fully automating this boring and tiring task.

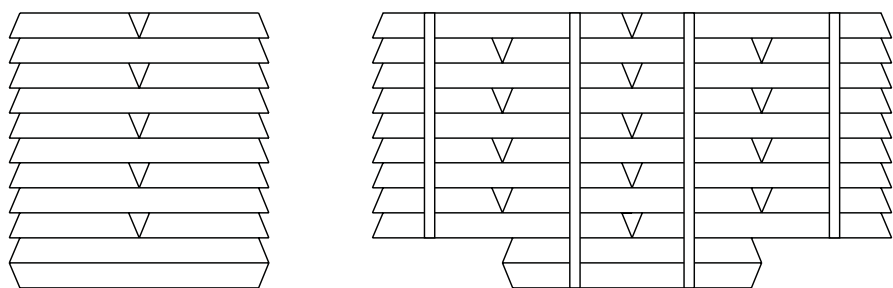
An important reason for efficient skimming is that dross remaining on the slab surface as lumps or edge ‘flashes’ can interfere with the equipment stacking slabs into bundles, causing jamming and either a consequent stoppage of the casting line or the need for manual intervention to circumvent the automated handling equipment, resorting to manual stacking until the jam is removed. Interruption and stoppage of the line generally results in reject ingots on recommencement. Straight-line machines normally have up to 140 slab moulds each of 25 kg, with a casting capacity of around 15 tonne per operating hour.

At the discharge position, slabs have a temperature of around 300°C or less. Slower cooling of the free zinc surface relative to the sides and bottom of the mould is desirable to avoid surface cracking of the slab. Slabs are then further cooled on a conveyor that travels through a water bath, but should be designed to emerge above 120°C to ensure that no water is retained.

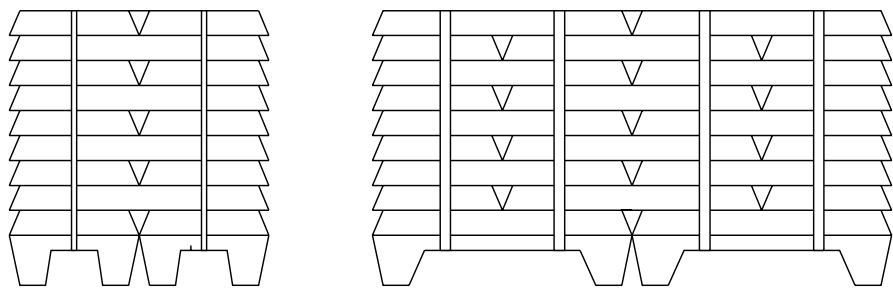
Slab Bundle Preparation

For handling and transport, slabs are usually prepared into bundles by stacking slabs to form a compact 1000 kg parcel. Robotic equipment is usually used for this operation and for the placement and tightening of straps that hold the bundle together. Typical bundle formats are illustrated in Figure 8.3. In forming the bundles, it is the practice, in some cases, to use separate slabs of a different shape for the base of the bundle or ‘foot slabs’. These are elevated to allow access by fork lift truck tynes beneath the bundle. A bundle will normally be made up of 40 to 25 kg slabs and four of these will be foot slabs, also of 25 kg weight. This formation will require the casting machine to include four different moulds in every 40 and the total number of moulds in the mould chain must be a multiple of 40, such as 120. It is also quite practical to construct bundles entirely from standard slabs, using four centrally located standard slabs forming a central foot – as shown in Figure 8.3.

Adequate tensioning of the bundle straps is critical to allow for retained heat and subsequent contraction on cooling. It is common practice to apply a compression load to the bundle during strapping for this reason, and to compress any small projections on the slabs that may hold them apart and allow the slabs to work loose during transport. Straps are usually high tensile steel, but do require corrosion protection to prevent rusting and staining of the product metal. Nylon or other plastic strapping has been used, but is generally less rigid and requires strong tensioning and retention of that tension to be effective.



1000 kg Bundle of Standard 25 kg Slabs



1000 kg Bundle of 25 kg Standard Slabs and Foot Slabs

FIG 8.3 - Format of slab bundles.

Shrink wrapping of the bundle in plastic film is also applied but must be used with caution, since it can cause ‘sweating’ or water condensation beneath the film, resulting in corrosion of the zinc and the formation of ‘white rust’ (basic zinc carbonate).

Block Casting

Output of metal in the form of one or two tonne blocks represents a growing percentage of total production, and is particularly used to supply large continuous steel sheet galvanising lines. Blocks are batch cast in individual water cooled steel moulds. Often moulds are fixed in position and are arranged either in an arc to be fed by a centrally pivoted swing launder, or are arranged in a straight line and fed by a sliding parallel launder system. Typical alternative layouts are shown in Figure 8.4. Operation is usually manual but more automated systems have been developed where large production tonnages can justify the capital cost, such as the Lewis Block Caster.

Molten zinc is poured into the mould from the feed launder to a preset level. The surface of the metal is then manually skimmed and the block is left to cool. It is common to cover the mould with a lid containing electric radiant heaters. This keeps the surface molten until final solidification, and prevents the formation of central shrinkage cavities. Such cavities can readily form in large blocks, dependent on their shape, and may fill with water if the block is exposed to the weather. On re-melting the block, such water inclusions can result in the explosive formation of steam with the highly dangerous eruption of molten metal from the melting bath. The avoidance of shrinkage cracks and cavities is therefore a critical issue in block casting.

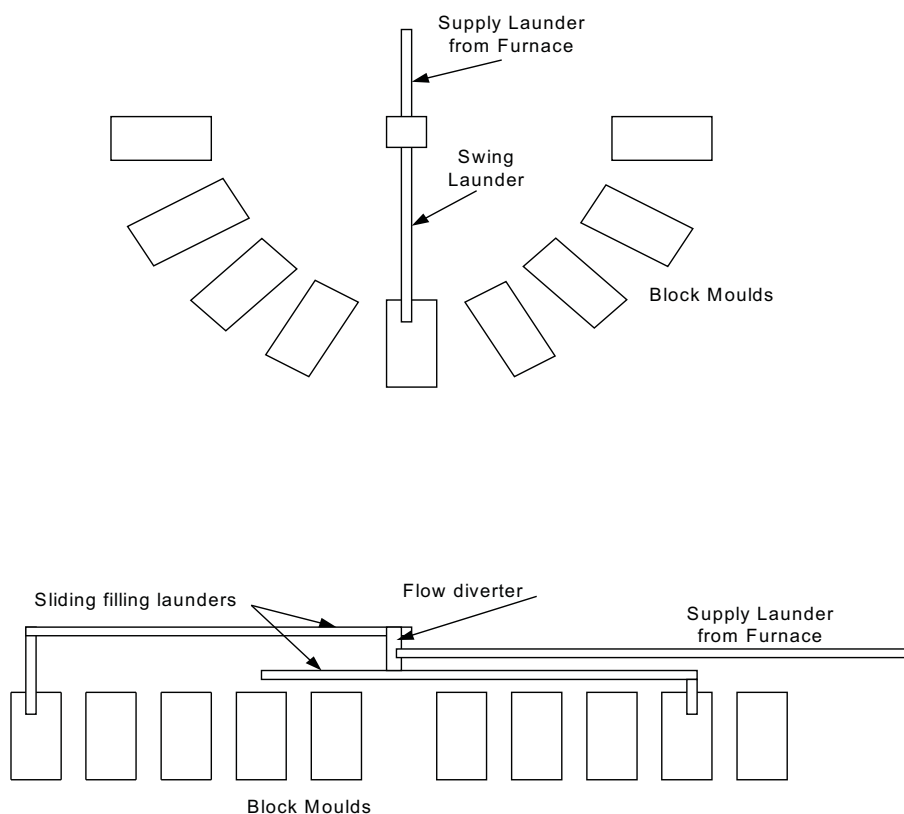


FIG 8.4 - Alternative block casting layouts.

Steel lifting lugs or pins are usually cast into the block to serve as attachments for a crane to lift the block from the mould. The lugs or pins may then be pushed out of the block using an hydraulic press and are returned to the mould. This will also leave holes or indentations in the block for later use as attachments for lifting and handling equipment, although they are normally designed for fork-lift truck handling. The cycle time for the casting of one tonne blocks is normally close to one hour.

Mould skimmings can be of the order of 15 kg per tonne and are a mixture of oxide dross and entrained metal. On re-melting, 85 per cent can be recovered as metal, leaving about 15 per cent, or 2.5 kg per tonne as oxide dross for recycle to the roasting plant. Dross formation and skimming requirements are greatly influenced by the method of pouring molten metal into the moulds. Overhead pouring generates considerably more dross than underflow pouring through a tube attached to the feed launder, which allows metal to flow to the base of the mould and fill upwards.

Continuously cast ingots are unusual in the zinc industry compared with the copper and aluminium industries. One exception is the ‘C Block’ produced by Cominco at Trail, British Columbia. This is a continuously cast section that is sawn into the required lengths and tonnage. It would appear that lower heat transfer rates from zinc due to available temperature differences mean that the productivity of such operations are significantly lower than for higher melting point metals, and it is not competitive with batch block casting for zinc. It does however produce a very high quality product in terms of appearance and dimensional consistency.

Labelling of ingots, bundles and blocks is important. The composition grade designation is usually cast into each slab as part of the mould, or can be stamped onto each ingot. Similarly grade designations can be stamped onto blocks. Both slab bundles and blocks also require labelling to indicate weight and production reference or lot numbers as well as product designation. Labels are usually printed automatically and bar coded when the bundle or block is weighed, and are glued onto the metal in a number of accessible locations.

Analytical Quality Control

The control of alloy composition and product quality is a vital component of the melting and casting operations. Metal is sampled in the molten form before casting and the sample is cast into a disc of around 50 mm diameter using a hand ‘book’ mould. The discs are machined to remove the surface and are analysed using spark or plasma emission spectroscopy. Spectrometers are direct reading and measure selected wavelength emission lines for individual elements as shown in Table 8.2. Since

TABLE 8.2
Emission spectrometer – analytical lines used.

Element	Wavelength mm	Element	Wavelength mm
Aluminium (1)	256.80	Magnesium	279.08
Aluminium (2)	266.04	Manganese	403.31
Aluminium (3)	396.15	Mercury	564.07
Antimony	231.15	Nickel (1)	341.48
Arsenic	234.98	Nickel (2)	352.45
Cadmium	228.80	Silicon	251.61
Cobalt	345.35	Silver	338.29
Copper	327.40	Thallium (1)	535.05
Chromium	425.43	Thallium (2)	351.92
Gallium	403.30	Tin	317.50
Indium	451.13	Titanium	323.45
Iron	371.99	Zinc (1)	213.86
Lead (1)	283.31	Zinc (2)	334.50
Lead (2)	368.35		

absolute line intensity can vary from one alloy to another as influenced by other elements present, the instrument provides a comparative measure only and it is important to calibrate against high and low standards for each measurement. A wide range of standards for each alloy produced needs to be prepared as a set of standard discs.

Sampling frequency depends on the particular alloy and its normal variability. It may require one sample every tonne or every ten tonne cast, and needs to be established by proper statistical analysis. Statistical Process Control methods should be used for production with control charts showing action and reject limits. Rejected lots are recycled back to the alloy preparation stage and appropriate changes are made to additions to compensate for the departure from specification.

Cathode zinc should also be sampled at least on a daily basis. This is done by punching discs from the zinc sheet at random locations. The punchings are melted and cast into discs for analysis.

All sampling must be done carefully with conscious recognition of the potential for bias due to impurity segregation or other means. Segregation can occur in the disc mould if the casting solidifies too slowly, and rapid chilling of the mould is preferred for this reason.

ZINC DUST PRODUCTION

Fine zinc powder is required for solution purification and represents a recycle of up to five per cent of total cathode production depending on impurities present.

Traditionally zinc dust is produced by atomising a falling stream of molten zinc with compressed air. Molten zinc flows from a hole in the base of a small crucible, which should be maintained at a constant level and temperature by circulation of molten metal from a holding furnace. The air atomising nozzle may consist of a number of directional air jets to ensure adequate coverage of the atomisation zone and to reduce the breadth of the size distribution of the resulting zinc dust produced. The average particle size of the zinc dust produced can be regulated by the pressure of the compressed air supply.

Dust is collected in a large settling chamber, and the product is screened over a number of different aperture rotary deck screens for classification. In many instances, the coarser dust may be used in one stage of the purification sequence (such as copper cementation) and the finer fractions used in other areas. Oversize may be re-melted. Zinc dust is usually transported to the purification operations using transportable batch hoppers.

It is also possible to use water for zinc dust atomisation, which greatly simplifies collection and delivery to the solution purification plant as a slurry. However, this method produces a relatively coarse dust and may not be suitable for some purification techniques, which require dust below 20 microns for adequate reaction rates and for efficient utilisation.

The presence of lead in zinc dust can have some advantage in cementation removal of impurities, and hence can provide an outlet for any zinc containing high levels of lead.

Material Balance Control and Effluent Treatment

PURPOSE

Apart from the control of process conditions such as temperature, pH and oxidation potential, material balance control is critical for the stable operation of the hydrometallurgical circuit. This ensures that critical concentrations of zinc, sulfuric acid and impurity elements are all kept at required levels with a high degree of stability, and allows for the optimum performance of the electrolysis stage as well as solution purification operations.

Since the prime purpose of the circuit is to extract zinc as high purity cathode, clearly separate outlets must be provided and controlled for all other elements entering the hydrometallurgical circuit. The roasting operation serves to separate some impurity elements prior to the leaching stage, and thus reduces the amount of these elements entering the solution circuit from raw concentrates. This particularly applies to chlorine, fluorine, mercury and selenium. These elements are separated from roaster gas prior to sulfuric acid production in the gas cleaning section, and exit the process in a weak acid bleed solution from the gas cleaning.

Chapters 5 and 6 have detailed how many elements harmful to zinc electrowinning are removed in leach residues or from solution purification operations. In addition, outlets must be provided for other materials that are not directly harmful to electrolysis. In particular, control is required over water and sulfate balances to maintain fixed solution inventories and the concentration of zinc and sulfate in circuit solution.

IMPURITY OUTLETS

Some impurity elements can be separated from the solution circuit as by-products such as:

- copper as a cementate;
- nickel and cobalt as cementates for further processing;
- cadmium as high grade metal;
- lead, silver and gold concentrated into a leach residue suitable as feed to a lead smelter;
- calcium and sulfate as gypsum;
- mercury as mercury (I) chloride (calomel) from roaster gas cleaning; and
- in special circumstances where quantities are sufficient for economic recovery – selenium, germanium, gallium and indium as concentrates for further processing.

Other bulk impurities such as iron and silica are eliminated as waste leach residues and can provide a suitable carrier and scavenger for many minor elements, particularly arsenic, antimony, germanium, and thallium. Iron can also remove potassium and sodium by forming jarosites under suitable conditions and, in hydroxide form, can scavenge fluorine. Manganese is primarily separated and controlled by removal as anode sludge.

Sulfate input largely arises from the presence of zinc sulfate in calcine or from direct sulfuric acid additions. Higher roaster operating temperatures will reduce the level of zinc sulfation in calcine collected from the roaster itself, but the level of sulfate present is higher in calcine collected by separation from roaster gas in the boilers and beyond, where gas temperature is reduced and sulfation can occur. Air leakage into the gas system providing extra oxygen and cooling can aggravate sulfate

formation. A high proportion of calcine carryover from the fluid bed roaster to the boiler will thus give rise to higher levels of sulfation in the composite calcine product. This will clearly vary depending on roasting conditions and the reactivity and nature of the concentrates.

There are often also some direct inputs of sulfuric acid into the solution circuit for various reasons, but particularly when a high sulfate content residue such as jarosite is produced, or where there are other excessive losses of sulfate in other residues. In these cases, acid addition will be needed as a control to maintain circuit balance. Otherwise there will be a need to discard sulfate, which will occur through the separation of gypsum either directly or in leach residues, and through the loss of solution as entrainment or as a direct bleed.

Highly soluble elements remaining in solution, such as magnesium and chlorine, as well as sulfate and water, can be discarded from the circuit in the form of a solution bleed. This provides a key control for these elements and in some instances for water balance.

Water Balance Issues

The maintenance of a steady zinc concentration in purified solution and a steady solution inventory are key issues for process control. Changes in zinc concentration in solution will necessitate corresponding changes in solution flow rates for constant zinc production. Since there are limits to the equipment and a need to maintain steady flows to ensure suitable residence times in various processing stages, as well as steady operation, it is essential that zinc concentrations are stable. Generally, the amount of acid produced in spent electrolyte will directly relate to the zinc deposited as cathode metal and in turn will control the input of calcine into the leaching operation. If sulfate inputs and outputs are in balance, then the only cause for changes in zinc concentration will be a change in solution inventory resulting from a lack of water balance control. If the sulfate balance is not adequately controlled, there are dangers of excessive solution inventories without variation in zinc concentration. High solution inventories will reduce buffer storage capacity and the ability to accommodate interruptions to solution flow due to equipment failure and maintenance. If this causes interruption to the electrolysis section, production will usually be irretrievably lost.

The maintenance of a satisfactory water balance is important for stable operation and it is best achieved by operating normally with a net water deficit. That is where the loss of water through evaporation from electrolyte cooling, plus any bleed streams, exceeds inputs from residue washing, steam injection, pump seal water, etc. Water balance is then controlled by direct process water additions to maintain solution inventory and zinc concentrations. This can be done by monitoring zinc concentration in purified solution as well as by solution density.

SOLUTION BLEED PROCEDURES

Entrainment of plant solution in leach and iron residues provides an effective bleed of solution and impurities from the electrolyte circuit, but also represents a loss of soluble zinc. Washing of residues to reduce zinc loss together with the recycle of the wash solution will correspondingly recycle soluble impurities and reduce the outlet of these elements. Hence, this form of outlet for impurity elements carries the cost of associated zinc losses and is not suitable as a major control procedure. In the absence of a direct solution bleed it is often the practice to control water balance by varying the amount of wash water used for washing leach and iron residues. This is inefficient in terms of overall zinc recovery.

Zinc Stripping From Spent Electrolyte

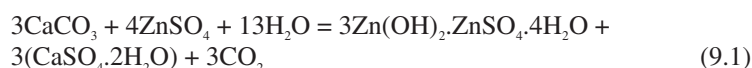
Efficient control of material balances by solution bleed requires the discard of solution from which zinc has been depleted. Two methods are commonly used. In the first method, bleed solution as spent electrolyte is passed through additional electrolytic cells to strip zinc down to low levels of less than 5 g/L. As indicated in Chapter 7, electrolytic cell operation at low zinc to acid ratios will result in low

current and power efficiencies, and for a zinc concentration of 5 g/L with a corresponding sulfuric acid concentration of 225 g/L in the final electrolyte, the current efficiency would be less than 50 per cent. With the use of a number of cells in series, the overall current efficiency could be raised and may be around 70 per cent.

The resulting stripped electrolyte is sent to an effluent treatment plant. With the use of stripping cells in series, it is difficult to operate a conventional circulating electrolyte and evaporative cooling circuit, and attention needs to be given to appropriate cooling such as the addition of cooling coils in the cells or operation at reduced current densities.

Selective Zinc Precipitation

The second method for discard solution treatment involves the selective precipitation of zinc from impure leach solution as a basic zinc sulfate at a pH of between six and seven (Matthew, Newman and Palmer, 1980). Lime or ground limestone is commonly used for neutralisation and since the required pH can be achieved using limestone, this is preferred. The reaction proceeds according to Equation 9.1.



The solids separated by filtration consist of mixture of basic zinc sulfate (BZS) and gypsum and can be returned to the leaching section to re-dissolve its zinc content. In fact the neutralising capacity can be used to good effect by addition to the iron precipitation stage. The basic zinc sulfate is dissolved and the gypsum remains and is removed with the iron residue. Alternatively, the precipitate can simply be leached in spent electrolyte to give a separate gypsum by-product. The residual solution or filtrate is sent to effluent treatment. A flow sheet for basic zinc sulfate precipitation or the 'Basics Process' is shown in Figure 9.1.

The selectivity of zinc separation from solution and from other elements such as manganese, magnesium and chlorine in the Basics Process is pH dependent. Table 9.1 shows the recovery of these elements into a Basics precipitate (Matthew, Newman and Palmer, 1980).

TABLE 9.1
Recovery into precipitated basic zinc sulfate.

pH	Zn Recovery	Mn Recovery	Mg Recovery	Cl Recovery
6.0	78.1 %	3.8 %	10.9 %	0.7 %
6.3	91.3 %	8.2 %	13.7 %	1.5 %
6.6	96.6 %	17.7 %	17.2 %	3.3 %
7.0	99.0 %	49.8 %	23.3 %	9.3 %

Depending on the need to discard manganese in particular, the ideal operating pH is probably around 6.5. High operating temperature is beneficial for the Basics Process in terms of reaction rates, limestone utilisation efficiency and assisting the filtration operation. An operating temperature of 95°C is usually specified and can be achieved by direct steam injection into the reaction vessel. Operation on a diluted solution of less than about 90 g/L zinc content is also preferable due to the high solids loading and proportion of solution entrained in the filter cake, which will necessitate extensive washing to achieve effective discard of soluble components. Because of this, it can be advantageous to use the Basics Process to treat wash solutions from leach residue or iron residue filtration. In this approach, the filtrate from the Basics Process can be reused as wash water as illustrated in Figure 9.2. This will recover and recycle zinc to the plant circuit and allow soluble impurities remaining in basics filtrate to

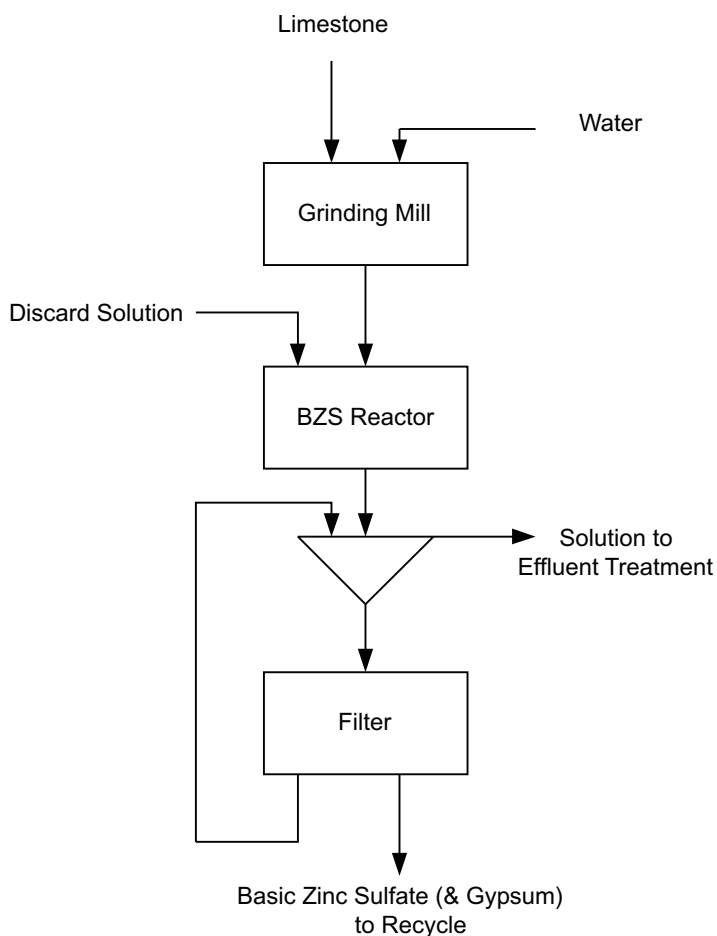
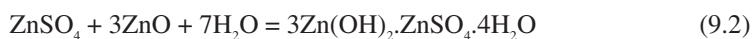


FIG 9.1 - Selective zinc precipitation as basic zinc sulfate.

be discarded as entrainment in the washed residues. Otherwise, the basics filtrate can be directed to an effluent treatment plant.

Calcine may be used for basic zinc sulfate precipitation in accordance with the reaction given in Equation 9.2.



The reactants tend to coat the zinc oxide surfaces and block the reaction, hence the use of calcine can be relatively inefficient. This also requires the use of finely ground calcine to provide maximum surface area as well as intense agitation in the reaction vessel. It has been found that the use of fine calcine collected in boilers and the gas train is not effective due to its high degree of surface sulfation, therefore it is preferable to use finely ground bed overflow calcine from the fluid bed roaster. Although the use of calcine does not incur the production of gypsum, four moles of zinc must be handled and reprocessed for each mole of zinc recovered from solution, which can be a disadvantage depending on where the basics precipitate is used. It can impose large circulating loads.

In general, the use of limestone is simpler and the sulfate balance control can be an advantage. For this reason, it is the usual method of application of the Basics Process.

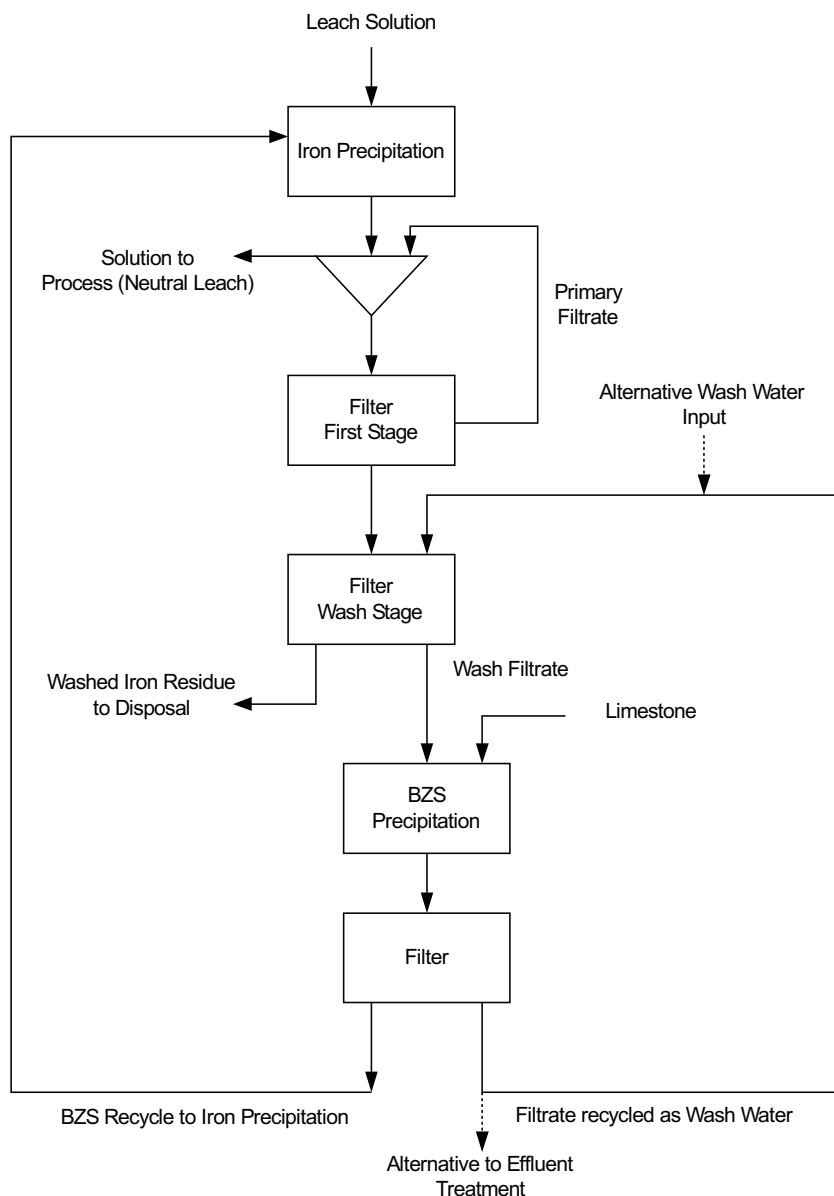


FIG 9.2 - Integration of basics with iron residue washing to provide a solution bleed.

LIQUID EFFLUENT TREATMENT

An electrolytic zinc plant produces a number of liquid effluent streams that require treatment to remove metals and other regulated elements before discharge to the local environment. The standards to be met for discharged liquid effluent will vary considerably depending on local regulations and the nature of the receiving environment.

Typical limits for key elements in discharged waste water are given in Table 9.2, but may vary significantly from these figures at any particular location.

Principal effluent streams are:

- roaster gas cleaning – weak acid bleed solution;
- zinc electrolyte bleed – usually as spent electrolyte from zinc stripping cells or following basic zinc sulfate precipitation;
- general plant spillage and drainage from equipment cleaning;
- plant area stormwater run-off; and
- stockpile area run-off.

There are many effluent treatment strategies depending on particular circumstances, but if it can be generalised, effluents may be grouped into two broad categories for separate handling approaches.

- A. Dilute streams that do not contain deleterious impurities and can be recycled to the zinc plant solution circuit.
- B. Effluents containing impurity elements that represent outlets from the plant circuit and should not be returned.

Category A effluents may be separately collected in ponds and can be used as process water after neutralisation of any acidity. The total proportion of effluents in this category should be maximised so as to minimise the requirements for effluent processing and generation of associated solid wastes.

Category B effluents are predominantly weak acid bleed solution from roaster gas cleaning and zinc electrolyte bleed. This requires neutralisation and processing to remove all regulated elements – mainly zinc, cadmium, manganese, mercury, selenium and fluoride. It is generally the case that alkali metals, chloride and some sulfate can be tolerated in discharged effluent within set limits, and provides the outlet for these elements.

The usual treatment procedure involves lime neutralisation to a pH of around ten often coupled with a sulfide precipitation polishing stage to scavenge base metals to low levels. Lime neutralisation may be conducted in two stages; first to a pH of up to four to neutralise free acid and to produce a relatively clean gypsum for sale as a by-product, followed by a second high pH stage and sodium sulfide addition to produce a contaminated gypsum. This approach significantly reduces the quantity of final effluent treatment solids for disposal. A generalised flow sheet for a typical lime neutralisation effluent treatment procedure is given in Figure 9.3. Critical operating features of the lime neutralisation plant are the settling and filtration characteristics of the final solids, which require careful pH control and the use of flocculants.

In some situations, effluent treatment solids can be re-leached with acid to extract zinc but this will extract any precipitated magnesium. If this approach is adopted, a lower pH should be used in effluent treatment to limit the amount of magnesium precipitated. The resulting gypsum may then be suitable for sale. There will also be the danger of recycling excessive fluoride and this approach is not particularly robust due to the degree of compromise required.

The quantity of sulfuric acid contained in the weak acid bleed from gas cleaning largely results from SO₃ formation in the boilers and can be significantly increased by air leakage into the roaster gas handling system, which operates under slightly negative pressure. In the interests of reducing the load on the effluent treatment facility, and the quantity of gypsum produced, it is beneficial to minimise air leakage and maintain a relatively ‘tight’ gas system.

TABLE 9.2
Typical discharge water standards.

Element	Typical Limit mg/L
Zinc	5.0
Copper	1.0
Cadmium	0.03
Manganese	0.5
Arsenic	0.25
Mercury	0.01
Selenium	0.02
Thallium	0.01
Chlorine	250
Fluorine	2.0

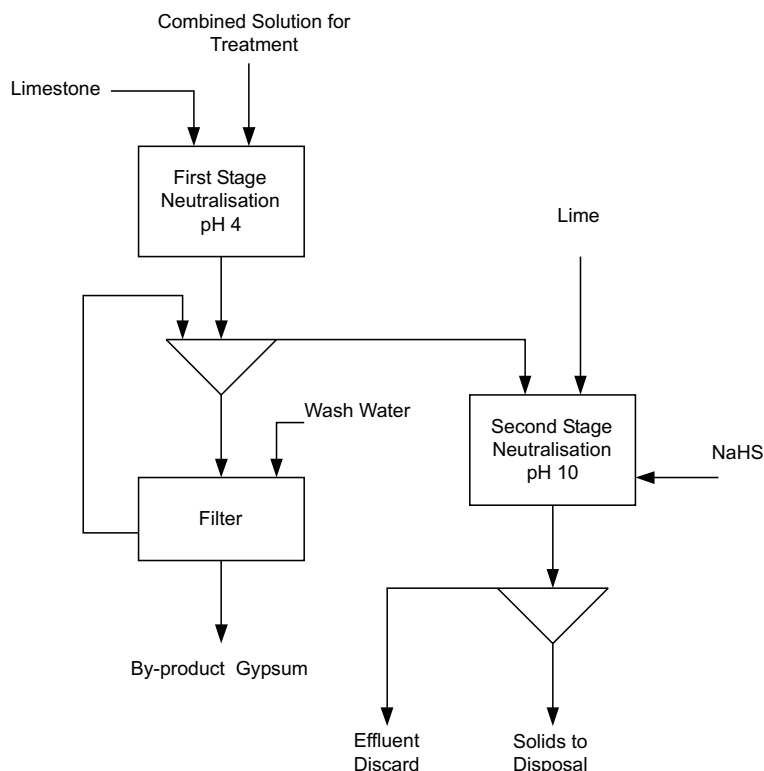


FIG 9.3 - Generalised effluent treatment – using lime neutralisation.

There are many variations to this standard approach and different neutralisation reagents can be used to reduce the quantity of solids. Calcine may be used for the initial acid neutralisation and caustic soda/ sodium sulfide for the final neutralisation to precipitate base metals. Calcium chloride may be added in the final stages to precipitate fluoride as CaF_2 .

The use of sulfur reducing bacteria has been applied at the Budel smelter in the Netherlands (Copini, Janssen, Buisman and Vellinga, 2000). In this case, sulfur reducing bacterial growth is promoted in the effluent stream, which produces H_2S , precipitating metals as sulfides. The sulfide precipitate can be separated and recycled to the roasters. Further treatment of the resulting effluent has been necessary in this case to remove fluorine. This treatment uses calcium chloride to precipitate calcium fluoride in a relatively high grade form as a by-product. This approach using sulfur reducing bacteria can process effluent with minimal waste solids, but does involve a significantly greater capital and operating cost.

Disposal of the final effluent treatment solids follows many avenues. It may be mixed with iron residues such as jarosite or goethite for disposal in ponds, or for further pyrometallurgical processing. Otherwise it can be placed in separate sealed ponds or sent to toxic land fill. The key issue is to maximise recycle of effluent streams without adverse impact on the electrolytic zinc process and to confine the output of waste elements to the minimum volume of solid waste.

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Other Electrolytic Processes

GENERAL COMPARISONS

The large scale commercial development of the electrolytic zinc process has been almost exclusively based on the sulfate system. The reasons for this are numerous and practical and may briefly be summarised as follows:

- Sulfuric acid as a leaching agent is compatible with the treatment of sulfide raw materials and is normally a large volume by-product. The sulfate ion is also highly stable.
- Smooth strippable electrolytic zinc deposits can be easily produced from sulfate solutions.
- The formation of oxygen at the anode enables the use of a simple open cell and the release of oxygen to the atmosphere.
- The limited solubility of lead allows for its ready separation and also allows for the use of low cost lead anodes.
- The limited solubility of calcium sulfate allows for separation and control of the sulfate balance in solution.
- Sulfuric acid and its salts have negligible vapour pressure and containment is not an issue.
- Corrosion of equipment is manageable without high cost for sulfuric acid and sulfate systems in comparison with other systems.

Alternative systems for zinc hydrometallurgy and electrowinning, which have been evaluated in some detail, have largely been based on chloride or alkali electrolytes. Although these systems have been evaluated over many years with many process options, there have been no substantial commercial developments. The following attempts to provide a brief overview of some of the features and issues associated with these alternative systems.

CHLORIDE SYSTEMS

As mentioned in Chapter 2, some of the first development efforts of electrolytic zinc production were based on the chloride system with some plants being operated for a number of years. In particular, the Hoepfner Process operated in England from 1897 to 1924.

With the chloride system there are two broad alternatives involving either aqueous electrolysis of zinc chloride solution, or molten salt electrolysis. Zinc chloride may be produced by hydrochloric acid leaching of roasted concentrates, or by chlorination of zinc sulfides either directly using chlorine, or indirectly using ferric chloride as a carrier.

Since chlorine is produced at the anode during electrolysis the use of chlorination has attractions in providing a closed system. If prior roasting is employed, sulfuric acid must be produced from roaster gases as for the conventional process, and hydrochloric acid for leaching must be separately supplied or produced from chlorine.

One of the significant disadvantages of chloride systems has been the severe corrosion aspects and the need for expensive materials of construction, as well as the high cost of maintenance. An advantage is the higher reaction rates generally encountered with chloride systems enabling the size of reaction equipment to be reduced. To some extent, this compensates for the higher cost of construction materials to handle chlorine and the highly corrosive chloride solutions.

Calcline Leaching Processes

If oxides or calcine are used as the starting feed material, a zinc chloride solution can be produced by leaching with hydrochloric acid. The solubility is high and hence higher concentrations of zinc in solution are possible than with the sulfate system.

The resulting leach solution can be purified in a similar manner to the sulfate system with oxidation precipitation of iron followed by zinc dust addition to cement out other impurity metals. Lead and silver may be recovered by cementation or can be partly precipitated as sulfates.

It has been found that iron may be separated as ferric oxide from a high concentration zinc chloride solution by treatment with zinc oxide and oxygen. Manganese is also simultaneously removed (Monk and Fray, 1976).

Electrolysis of the purified solution will generate a solution depleted in salt content, since zinc is deposited on the cathode and chlorine on the anode. To maintain solution conductivity, an inert solute such as sodium chloride is usually used at a level of around two molar. Spent electrolyte recirculated to the leaching stage will require the addition of hydrochloric acid. This may be generated from cell chlorine by reaction with hydrogen or steam. Alternatively, if there are markets for the chlorine as a by-product, hydrochloric acid can be generated by reaction of sulfuric acid (produced from roasting), with common salt. This would leave a sodium sulfate waste product. The regeneration of hydrochloric acid adds considerable complexity. Alternatives such as direct chlorination, which also avoid roasting, are preferable. The EZINEX Process (Olper, 1998) also enables hydrochloric acid to be generated in the electrolytic cells and is discussed below.

Direct Chlorination

Zinc sulfide as zinc concentrate can be directly leached with chlorine to produce zinc chloride and elemental sulfur according to Equation 10.1.



The chlorination can be carried out dry at elevated temperature (600°C) with volatilisation of the free sulfur. Alternatively, it can be conducted in an aqueous system to give a solution of zinc chloride and a leach residue from which sulfur can be recovered by flotation, followed by melting of the concentrate and filtration.

The US Bureau of Mines developed a wet chlorination procedure (Haver *et al*, 1976), operating at 100°C and 3 atm pressure, followed by the addition of oxygen under pressure to precipitate iron from solution as ferric oxide. The resulting zinc chloride solution is separated by filtration and is purified by zinc dust cementation in preparation for electrolysis or for separation of solid pure zinc chloride by crystallisation.

Ferric Chloride and Cupric Chloride Leaching

As an alternative to direct chlorination, ferric chloride can be used for direct leaching of the zinc sulfide concentrate at atmospheric pressure. This procedure is similar to ferric sulfate leaching as discussed in Chapter 5.6, but with greater efficiency in elemental sulfur formation and with higher reaction rates. Ferric chloride may be generated in the anode compartment of an electrolytic cell to avoid direct generation of chlorine. However, care must be taken to avoid any transfer of ferric ions to the cathode and subsequent reduction and loss of current efficiency for zinc deposition. For this reason, a diaphragm cell should still be used. An example of ferric chloride leaching applied to a range of base metal sulfides is the Canmet process (Craig *et al*, 1989).

Cupric chloride is also an effective leaching agent as an alternative to ferric chloride, and is the basis of the Cuprex process (Dalton *et al*, 1987) or its zinc equivalent – the Zincex process – and the Intec process (Everett and Moyes, 1992). These approaches use the cupric/cuprous couple for direct leaching of sulfides, and use chlorine for the conversion of cuprous to cupric ions.

Other Direct Leaching Systems

There are other aqueous chloride leaching methods such as the CENIM-LNETI Process (Figueiredo *et al*, 1993), which is based on an ammonium chloride solution and oxygen pressure leaching. In this process zinc is transferred by means of solvent extraction from the chloride leaching system to a sulfate system for conventional electrowinning. This was discussed in Chapter 5.

ELECTROLYSIS OF AQUEOUS ZINC CHLORIDE

Zinc chloride has a very high solubility and high conductivity, but if depleted during electrolysis another inert salt is necessary to maintain conductivity. This differs from the sulfate system where sulfuric acid is generated at the anode and raises the conductivity of the electrolyte. Usually sodium chloride is used as the added salt at a concentration of between one and two molar and the electrolyte is thus a mixture of the two salts. Hydrochloric acid also significantly raises conductivity, and the pH of the electrolyte may be held at around 2.0 to 3.5 with its addition. However, this does raise the potential to form hydrogen at the cathode and hence lose current efficiency.

The theoretical electrode potential for zinc chloride electrodecomposition is 2.11 V, which is higher than the corresponding value for zinc sulfate electrolysis at 1.99 V. The anode overvoltage is lower for chlorine formation than for oxygen formation, leading to an overall voltage for the chloride system at about 0.5 V lower than for the sulfate system. However, the use of diaphragms or membranes to separate the anode compartment for chlorine collection will raise cell voltage and raises energy consumption to levels comparable with the requirements for sulfate electrolysis. This generally eliminates any significant energy advantage for the chloride system. Limiting currents for zinc are higher for the chloride system allowing for higher current densities, which can again raise energy consumption but reduces cell area requirements.

Aluminium electrodes are used for the cathode, although corrosion can be severe and titanium may be preferred. Graphite or Dimensionally Stable Anodes (DSA) are used for the anode where chlorine is released.

Zinc deposits from a chloride solution tend to be dendritic and organic smoothing agents are generally required. Gum arabic has been used, but tri-butyl ammonium chloride (TBACl) appears to be favoured at levels in the range of 20 to 40 mg/L.

The collection of gaseous chlorine is a significant complication requiring a compartmented cell with sealed anode compartment for chlorine collection and an open cathode compartment to allow easy access to the cathodes for lifting and stripping. It is possible to capture the chlorine as an active species in solution or in suspension without gas evolution. The Intec process (Everett and Moyes, 1992) uses an interhalogen compound with bromine – BrCl_2^- termed 'Halex' as a collector. This is formed at the anode according to the reaction given in Equation 10.2.



The Halex compound in the anolyte is circulated to the leaching stage where it can be used for direct chlorination. The electrolyte matrix may contain 280 g/L NaCl and 12 g/L NaBr.

With cell operation at low temperatures of less than 9°C it is possible to form a chlorine hydrate as a solid suspension in the anolyte and similarly circulate that to the leaching stage for use in direct

chlorination (Fray and Thomas, 1980). In this case, the cell would need to be cooled using a refrigeration system such as cold brine in cooling coils, which adds significant complication and cost.

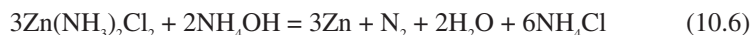
An approach which avoids the complications of chlorine evolution and generates HCl for zinc oxide leaching has been developed by Engitec Impianti SpA as the EZINEX Process (Olper, 1998). This process uses an ammonium chloride/zinc chloride electrolyte with ammonia as the reactive species and proton donor during leaching. Leaching follows Equation 10.3.



The resulting solution can be purified by cementation with zinc dust and then electrolysed in a standard open cell. Ammonia is consumed in the anode reactions and is added to the cell to maintain a pH of 6.0 to 6.5. Anode reactions are understood to involve the formation of chlorine according to Equation 10.4, which immediately oxidises ammonia to nitrogen and generates HCl in accordance with Equation 10.5.



The overall electrolysis reaction is then given by Equation 10.6.



The spent electrolyte is recycled to the leaching stage.

Due to the depolarising effect of the anode reactions, overall cell voltage is relatively low in comparison with other cells and power consumption is correspondingly lower at around 2560 kWh/t of cathode zinc. However this comes at the expense of ammonia added at the rate of about 180 kg/t of cathode zinc.

The EZINEX Process is most suited to the treatment of zinc oxides, and was developed for the processing of electric arc furnace dusts from secondary steel production. One significant disadvantage though is the fact that ferrites are not dissolved by the leaching reactions and pre-reduction of the feed is necessary or separate treatment of the leach residue.

The Zinclor process and Zinclor cell were developed by Tecnicas Réunidas SA and integrate a solvent extraction system using a series of solvents capable of transferring zinc chloride from one solution to another. (DPPP or dipentyl pentylphosphonate by Bayer and ZNX50 by Zeneca). High purity zinc chloride can be transferred from leach solutions to a high purity electrolyte from which zinc and chlorine are produced by electrolysis. Chlorine is returned to the leaching stage.

The Zinclor cell uses titanium cathodes and DSA anodes and includes either an ion exchange membrane or a simpler diaphragm. Cell electrolyte contains 65 g/L ZnCl_2 , 160 g/L NaCl and 3 g/L HCl. Gum Arabic is the preferred smoothing agent and requires a dosing level of around 350 g/t of cathode zinc.

Performance is similar to the sulfate system at similar current densities of 400 amps/m², with a cell voltage of around 3.2 V and energy consumption around 2900 kWh/t of cathode zinc at a current efficiency of 93.5 per cent (Diaz *et al*, 1993)

ELECTROLYSIS OF MOLTEN ZINC CHLORIDE

Pioneering work by E A Ashcroft in the 1890s on zinc electrolysis focused on molten zinc chloride. This process was unsuccessful, but various attempts have been made subsequently to develop this approach.

The advantages of molten salt electrolysis over aqueous electrolysis are the direct production of molten zinc, eliminating the need for cathode handling and stripping, and the avoidance of a diaphragm cell for chlorine collection. Early work failed due to impurities and the formation of basic salts or oxide sludges arising from reaction with refractories or from hydrolysis due to moisture absorption during processing and handling of zinc chloride.

Molten zinc chloride can be formed from direct chlorination of sulfides at high temperature, but is then heavily contaminated with other metal salts such as copper, lead and iron and is difficult to purify in that form. Generally process development has favoured aqueous leaching and solution purification followed by crystallisation of pure zinc chloride from solution. The salt must be dried and fed to the molten salt cell.

As indicated, hydrolysis can occur during the final stages of drying according to Equation 10.7.



The addition of HCl during drying can reduce the hydrolysis reaction.

The decomposition potential for molten zinc chloride is 1.629 V, corresponding with an energy consumption of 1334 kWh/t of cathode zinc, which is significantly lower than for aqueous sulfate electrolysis.

Zinc chloride alone is unsuitable for electrolysis since it has high vapour pressure (9.4 mm Hg at 500°C) and low conductivity ($0.09 \text{ ohm}^{-1}\text{cm}^{-1}$). It also tends to absorb water vapour and form basic salts as sludges. The addition of alkali metal chlorides can increase conductivity and lower vapour pressure. Conductivity is increasingly enhanced by KCl, NaCl and LiCl in that order, but the vapour pressure reduction and water absorption suppression is in the reverse order. A ternary system appears to give the greatest range of miscibility of molten salts, and the best compromise electrolyte composition for low volatility and fuming is a mixture of KCl, NaCl and ZnCl_2 . Zinc chloride levels range from 30 to 45 mole per cent and KCl from 25 to 55 mole per cent with the balance as NaCl. The activity of zinc chloride in the salt mixture will be somewhat lower than for zinc chloride alone, giving a higher theoretical energy consumption than noted above for the pure molten salt.

Operating temperature needs to be above the melting point of the salt mixture and of zinc metal, but needs to be kept as low as possible so as to minimise zinc chloride volatility and the back reaction of zinc and chlorine to reform zinc chloride. The back reaction is the primary cause of loss of current efficiency and is greatly dependent on the cell design and the separation achieved between zinc formed at the cathode and chlorine at the anode. For a simple cell design with a single cathode as a pool of molten zinc in the base of the cell, and with an upper graphite plate as anode, separation does not present a problem. Zinc will deposit on the cathode pool and chlorine will form on the anode plate and will rise as bubbles to the surface of the melt for collection from the gas space above the melt. In this case, current efficiencies of close to 100 per cent can be achieved. Other conceptual designs are based on the use of a stack of bipolar electrodes, with each electrode in the stack being a cathode on its upper surface and anode on its lower surface. Zinc and chlorine need to be channeled to collection points to avoid contact and maintain separation. This is more difficult and current efficiencies in more complex cells can fall to levels of around 95 per cent.

The formation and collection of oxide sludges in the base of the cell, interferes with the cathode and has caused difficulties in previous evaluations of this approach. The avoidance of oxide based internal cell refractories has been indicated as necessary and the use of nitride bonded silica or silicon oxynitride linings proposed. In addition, water absorption needs to be controlled at minimum levels by the salt mix selection and by control during zinc chloride drying.

If the cell is well insulated, heat generation should be sufficient to melt the zinc chloride feed. This amounts to 458 kWh/t of cathode zinc and adds to the theoretical energy for zinc chloride decomposition given above.

Actual reported energy consumption varies widely from 2600 to 8000 kWh/t of cathode zinc, depending on cell design (electrode spacing, etc) but more particularly on current density. The lower values correspond to current densities of around 1350 amps/m² and the higher energy consumption at current densities an order of magnitude greater. There are no clearly developed cell designs or definitive performance indications at the present time. However, because of the relative cost of cell construction, there will be a desire to operate at as high a current density as possible.

Productivity of a cell house in terms of floor area is one element of the associated capital cost of an electrolytic installation. The ratio of the actual cathode surface area of a modern electrolytic cell, for the standard sulfate system, to the floor area cross section of the electrode space is 35:1. Hence a single cathode molten salt cell will have to operate at 35 times the current density of the aqueous system to have the same productivity per unit of floor area. This would suggest current densities of the order of 15 000 amps/m² are required. The use of bipolar stacks could substantially reduce this requirement, but in order to achieve significant advantage in terms of installation size and cost it is suggested that current densities of at least 5000 amps/m² would be necessary with bipolar molten salt cells. Under these conditions it is likely that energy consumption for the molten salt system will significantly exceed that required for the aqueous sulfate system at 3000 kWh/t of cathode zinc.

In addition the problems of handling hot chlorine gas and maintaining adequate seals on the cell system are also most significant and have certainly worked against the commercialisation of this approach as a competitor to the standard method.

ELECTROLYSIS OF ALKALINE ZINC SOLUTIONS

As an amphoteric compound zinc oxide is soluble in sodium hydroxide (or potassium hydroxide) solution in accordance with Equation 10.8.



A leach solution of the order of ten molar with respect to NaOH is required to dissolve sufficient ZnO.

One advantage of this system is that iron and manganese are virtually insoluble and can be reduced to low levels by air oxidation. The leach solution can be purified by zinc dust cementation and electrolysed.

For electrolysis, the hydrogen overvoltage is higher than in an acid electrolyte allowing for improvement in the current efficiency of zinc deposition. The limiting current density for zinc is low at around 500 amps/m². However, there is a strong tendency for zinc to form powder, sponge or dendritic deposits from an alkaline electrolyte. The effective cathode surface area is greatly expanded, thus removing any constraint by the limiting current density, and practical current densities based on electrode area of 2000 amps/m² can be achieved.

Promotion of dendritic growth rather than powder or sponge forms is desirable and for this purpose magnesium cathodes are preferred rather than aluminium. Since the zinc will not redissolve in the electrolyte when detached from the electrode as in the acid sulfate system, the dendrites may be continuously scraped off the cathode and collected in the base of the cell for removal by pumping as a slurry. This provides for a fixed cell system without the need for cathode removal and stripping. As such it allows for clamped electrical contacts and much higher electrode currents than are possible with the conventional cell design. Enclosure of the cells and collection of oxygen for use in other processing steps is also possible.

The zinc slurry may be filtered and washed, then briquetted in preparation for melting. Oxidation losses of zinc on melting are likely to be significantly higher with this approach but are an offset for the significant advantage of a fully automated continuous cell operation.

The development of fluidised bed or spouted bed electrodeposition techniques has application in this context (Roy *et al*, 1998).

The reversible electrode potential for the $\text{Zn}/\text{ZnO}_2^{2-}$ half cell is -1.215 V, and for the OH^-/O_2 half cell is +0.401 V giving a reversible cell potential of 1.62 V. This compares with 1.99 V for the sulfate system.

Nickel anodes and activated titanium (DSA) have been applied, considerably reducing the oxygen overvoltage and hence total cell energy consumption. Indicative cell voltages are 2.5 V at comparable current densities to the standard sulfate system of 500 amps/m². At a current efficiency of 93 per cent this gives an energy consumption of 2200 kWh/t of cathode zinc, significantly less than for the sulfate system.

It is also possible to operate at current densities up to 1500 amps/m² at which level indicative cell voltage rises to 3.2, giving an energy consumption of around 2900 kWh/t of cathode zinc, comparable to the best performance from a modern sulfate system cell house but at three times the current density. On these indications there is potential for energy savings or capital savings from application of an alkaline system.

The disadvantage of the alkaline system is that it is based on oxide feed and that leaching will not attack zinc ferrite normally contained in roaster calcines. It would be necessary to use a two-stage roasting process with an initial oxidative roast to eliminate sulfur followed by a reduction stage operating at 750°C or above in which coal is added to hot calcine from the first stage to reduce zinc ferrite to ZnO and FeO. This would be a complication and additional fuel cost which will counter energy savings from the use of an alkaline electrolyte.

The concentration of zinc in solution is also low at around 30 g/L with sodium hydroxide levels at 240 g/L. This will require higher solution circulation rates and equipment volumes than for the sulfate system.

GENERAL APPRAISAL OF ALTERNATIVE ELECTROLYSIS SYSTEMS

Although alternative systems appear to offer significant advantages in some aspects of the electrolytic zinc process in comparison with the conventional sulfate system, there are usually offsetting factors and complications that reduce the overall apparent advantages to being relatively marginal when applied to the processing of standard zinc concentrates. In that context, the risks associated with departure from well-proven technology are high and consequently none of these alternative technologies has proceeded to large-scale commercial development.

Opportunities are more likely to exist for these alternatives with small scale specialised applications, such as the treatment of electric arc furnace dusts or for mineral concentrates with uncommon or high levels of particular impurities.

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PART C

CARBOTHERMIC REDUCTION PROCESSES

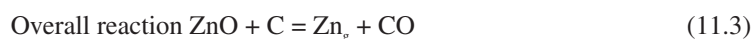
This part of the text covers the principal range of pyrometallurgical processes which predominantly utilise carbothermic reduction of zinc oxide to zinc metal. Production of zinc oxides as an intermediary material is also an important aspect of carbothermic reduction processes which are termed fuming processes in this context and are used for the recovery of zinc from low grade or secondary materials.

Chapter 11	Carbothermic Reduction – Process Chemistry
Chapter 12	Sintering
Chapter 13	Retorting Processes
Chapter 14	Blast Furnace Production of Zinc
Chapter 15	Thermal Refining of Zinc
Chapter 16	Zinc Fuming Processes
Chapter 17	Electric Furnace Processes
Chapter 18	Other Pyrometallurgical Processes

Carbothermic Reduction

CHEMICAL PRINCIPLES OF ZINC OXIDE REDUCTION

The direct reduction of zinc oxide materials was the initial approach to the commercial production of zinc metal and forms the basis of alternative production processes to the electrolytic process. Generally, reduction processes are based on carbothermic reduction according to Equations 11.1, 11.2 and 11.3:



where Zn_g represents zinc in vapour or gaseous form.

The equilibrium constants for the above reactions are:

$$K_1 = \frac{P_{\text{Zn}} * P_{\text{CO}_2}}{P_{\text{CO}}} \quad (11.4)$$

$$K_2 = \frac{P_{\text{CO}^2}}{P_{\text{CO}_2}} \quad (11.5)$$

The equilibrium constants may be calculated from the standard free energy change (ΔG°) for each reaction according to:

$$\Delta G^\circ = -RT \ln(K) \quad (11.6)$$

$$\text{and } \Delta G = \Delta H - T\Delta S \quad (11.7)$$

where ΔH is the enthalpy change and ΔS is the entropy change for a given reaction at temperature T degrees K. Enthalpy and entropy changes can be determined from the heat of formation of reactants and products at 25°C and can be calculated for different temperatures using heat capacity data from:

$$\Delta H = \Delta H^\circ + \int C_p \cdot dT \quad (11.8)$$

$$\Delta S = \Delta S^\circ + \int \frac{C_p}{T} dT \quad (11.9)$$

Generally, C_p is expressed as $a + bT + cT^2 + \frac{d}{T^2}$ and when applied to Equations 1.8 and 1.9 gives:

$$\Delta H = aT + \frac{1}{2} bT^2 + \frac{1}{3} cT^3 - \frac{d}{T} + I_h \quad (11.10)$$

and

$$\Delta S = a \ln T + bT + \frac{1}{2}cT^2 - \frac{1}{2} \frac{d}{T^2} + I_s \quad (11.11)$$

where I_H and I_s are integration constants which can be determined from standard enthalpy and entropy changes at 25°C (298°K). Hence, the free energy change for a reaction can be determined as a function of temperature from Equation 11.7.

Based on the thermodynamic data given in Appendix 1, the formulae for the carbon reduction reactions given in Equations 11.1 and 11.2 are:

$$\Delta G_1 = 206295 - 324.2 T + 29.075 T \ln T - 0.01571 T^2 + 2.335 \times 10^{-6} T^3 - \frac{456140}{T} \quad (11.12)$$

$$\Delta G_2 = 173616 - 120.1 T - 10.57 T \ln T + 0.01692 T^2 - 2.199 \times 10^{-6} T^3 - \frac{439320}{T} \quad (11.13)$$

Units are in joules per g mole and the corresponding value of the gas constant R in Equation 11.6 is 8.3143 J K⁻¹ mol⁻¹.

For a given temperature ΔG can be determined for each reaction and hence the corresponding value of the equilibrium constant K . The stoichiometry of a closed system requires that the oxygen contained in the CO and CO₂ present originates from ZnO and thus equates in molar amounts to the Zn vapour present (provided all zinc reduced is in the vapour form). Together with Equations 11.4 and 11.5 this enables the partial pressures of CO, CO₂ and Zn_g to be calculated with the results as illustrated in Figure 11.1.

Also shown in Figure 11.1 is the saturation vapour pressure of zinc above pure liquid zinc, taken from Equation 11.14:

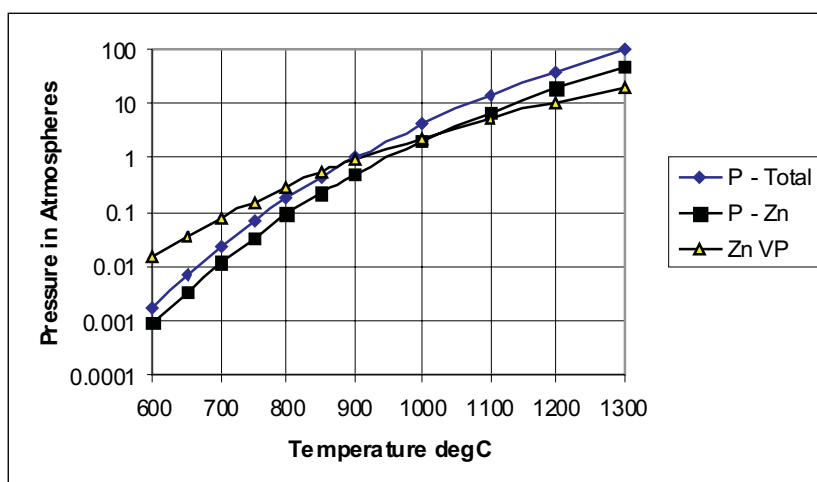


FIG 11.1 - Equilibrium vapour pressures - Zn-C-O system.

$$\text{Log } p_{\text{Zn}} = 5.227 - \frac{6163}{T} \quad (11.14)$$

where p_{Zn} is in atmospheres and T is in degrees K.

Liquid metal can only be present in the system if the vapour pressure of zinc from the reduction reactions exceeds the saturation vapour pressure of zinc. From Figure 11.1 the reaction zinc vapour pressure curve exceeds the liquid vapour pressure above a temperature of 1033°C and a zinc partial pressure of 3.22 atm with a total system pressure of 6.38 atm. To achieve any significant proportion of the zinc produced directly in liquid form, the operating conditions would need to well exceed these temperatures and pressures. In reality, high temperature systems cannot practically operate at high pressures, hence it is impractical to directly produce liquid zinc metal from a carbothermic reduction process. It is only practical to produce zinc in vapour form where it can be condensed to liquid by cooling the evolved gases.

Practical reduction systems operate at a total pressure of one atmosphere, and under this constraint the partial pressures of reaction products as a function of temperature will be as illustrated in Figure 11.2. In this case, the partial pressures of zinc and CO are almost equal and rise to 0.5 atm each at around 900°C. CO₂ partial pressure rises at around 900°C but is low and then declines. For a closed retort operating at 1000°C with excess carbon and 1 atm total pressure, the calculated gas composition will be:

Zn	49.96 %
CO	49.87 %
CO ₂	0.17 %

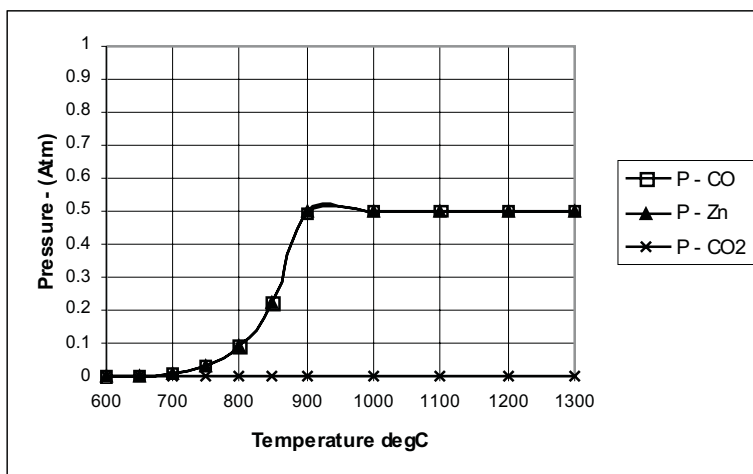


FIG 11.2 - Equilibrium vapour pressures (1 atm total pressure) Zn-C-O system.

If air is present in the carbothermic reduction process, such as when the blast furnace and heat are supplied internally by combustion of carbon, then the levels of CO and CO₂ will be substantially higher, significant levels of nitrogen will be present, and the zinc partial pressure will be much lower. For example, the standard ISF produces a gas at around 1000°C as feed to the condenser of the following composition:

Zn	6%
CO	18%
CO ₂	12%



Apart from the use of carbon, practical reduction can use hydrogen or hydrocarbons such as natural gas or methane.

For hydrogen reduction the reaction is given in Equation 11.15, and the equilibrium constant is given in Equation 11.16:



$$K_{15} = \frac{p_{\text{Zn}} \cdot p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \quad (11.16)$$

For a given temperature, the equilibrium constants can be calculated using thermodynamic data as for the carbon reduction example above, and the partial pressures for each component can be determined. For a system in which the total pressure is constrained to one atmosphere, the partial pressures are shown in Figure 11.3. The equilibrium pressures of zinc and water vapour will be the same as dictated by reaction stoichiometry.

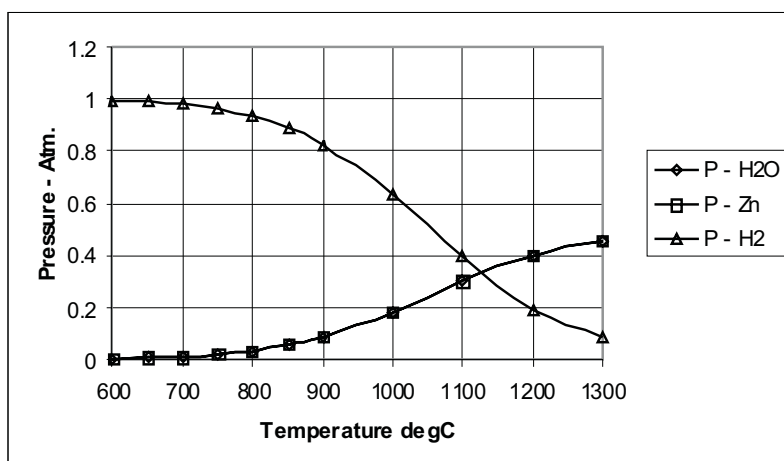


FIG 11.3 - Equilibrium partial pressures - hydrogen reduction.

For methane reduction, the initial reactions involve thermal cracking of the methane according to Equation 11.17, followed by the carbothermic reduction of ZnO in accordance with Equations 11.1 to 11.3. There is also potential for hydrogen reduction in accordance with Equation 11.15.



Reactions given in Equations 11.18 and 11.19 will also take place.



Using thermodynamic equilibrium data and stoichiometric balances, a series of simultaneous equations can be established and solved to determine the partial pressures of each component in the

system. For a system confined to one atmosphere total pressure, the results are illustrated in Figure 11.4. Figure 11.4 shows that cracking of methane initially takes place at lower temperatures before substantial reduction of ZnO, followed by reduction of ZnO with the carbon formed. The partial pressures of zinc and CO are almost equal, indicating that effectively no reduction by hydrogen takes place. The final gas mixture is essentially hydrogen at 50 per cent and zinc vapour and CO at close to 25 per cent each.

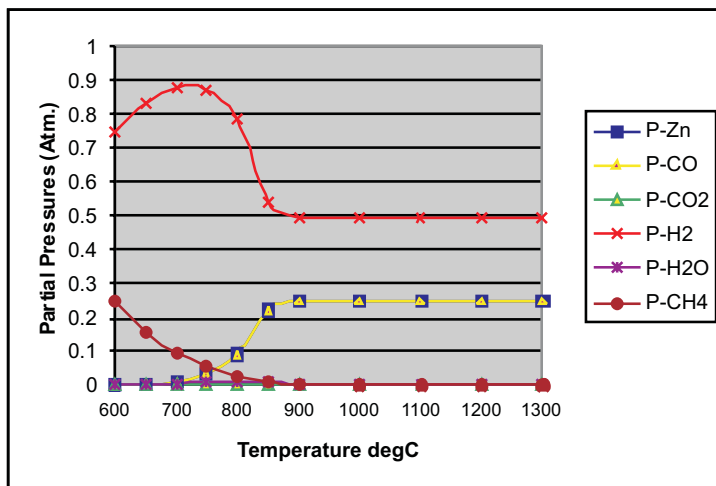


FIG 11.4 - Equilibrium partial pressures – methane reduction.

The approach outlined above for the calculation of system equilibrium as a function of temperature from basic thermodynamic data and stoichiometry is tedious, but can be greatly simplified by using computerised software packages now available, such as 'HSC Chemistry for Windows' developed by Outokumpu. The fundamental basis of calculation is the same, but simplicity and flexibility of use are greatly enhanced. The software provides a valuable tool for the metallurgist in the evaluation of process equilibria.

REDUCTION FROM MOLTEN SLAGS

Zinc oxide may be dissolved in a molten slag and reduced to zinc vapour by the addition of carbon or by the use of CO or natural gas. The composition of slags encountered in zinc metallurgy is varied and complex but in its simplest form is based on the ternary system $\text{CaO} - \text{FeO} - \text{SiO}_2$, with the addition of zinc oxide. The ternary phase diagram for this system is shown in Figure 11.5 giving the major solid phases and the liquidus temperatures at various positions on the phase diagram. The addition of zinc oxide will of course alter the characteristics and liquidus temperatures and practical systems are much more complex with significant amounts of Al_2O_3 and MgO . The properties of such systems have only been partly defined but attempts have been made (Jak *et al*, 1998).

The range of composition of common slags encountered such as lead blast furnace slags and a typical ISF slag are given in Table 11.1 and also shown in Figure 11.5. Normalised data assumes that only these components are present and add to 100 per cent.

In relation to the reduction of ZnO the same principles apply as outlined above, except that the activity of zinc oxide dissolved in a liquid phase may be significantly below a value of 1.0 taken for solid zinc oxide, as considered above, and will reduce as the concentration of zinc in the slag falls. This will significantly reduce the equilibrium zinc vapour pressure and Equation 11.4 may be re-written as Equation 11.20.

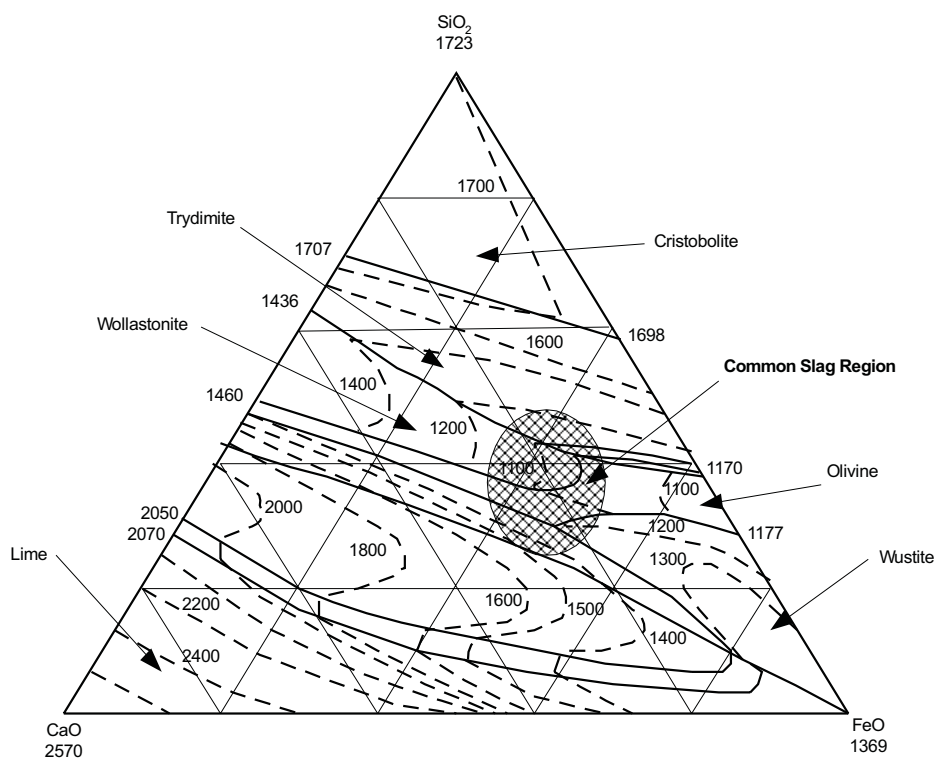


FIG 11.5 - Phase diagram system CaO-FeO-SiO₂ liquidus temperatures (Osborne and Muan, 1960).

TABLE 11.1
Typical slag compositions.

Component	Common Slags	Typical ISF Slag
SiO ₂	19 to 24 %	19.5 %
FeO	25 to 36 %	41.5 %
CaO	15 to 23 %	18.5 %
Al ₂ O ₃	2 to 10 %	8.0 %
MgO	1 to 5 %	0.5 %
ZnO	9 to 22 %	9.5 %
PbO	0 to 2 %	1.0 %
Normalised Data		
CaO	19 to 28 %	23.3 %
SiO ₂	23 to 44 %	24.5 %
FeO	31 to 44 %	52.2 %

$$p_{Zn} = \frac{K_1 \cdot p_{CO} \cdot a_{ZnO}}{p_{CO_2}} \quad (11.20)$$

where a_{ZnO} is the activity of ZnO dissolved in the slag.

The activity of ZnO can be related to the mole fraction of ZnO in the slag by the activity coefficient:

$$a_{\text{ZnO}} = \gamma_{\text{ZnO}} \cdot N_{\text{ZnO}}$$

where

γ_{ZnO} = activity coefficient of ZnO

N_{ZnO} = the mole fraction of ZnO in the slag.

Activity coefficients were initially calculated from the measured gas composition and partial pressures of Zn, CO and CO₂ using Equation 11.20 and assuming that equilibrium conditions prevailed. This led to the reporting of a wide range of activity coefficients from practical operations, and eventually to the conclusion that equilibrium conditions apply is not valid. Even with the use of hydrogen for reduction it has been difficult to achieve reliable measurements due to the need to estimate the amount of gas by-passing through the slag without opportunity for reaction. Electrochemical measurement methods have proved more reliable. A review and assessment of ZnO activity coefficients on this basis was given by Grimsey, Li, Hayes and Lee (1993), and is illustrated in Figure 11.6. This data is for a slag of 8.5 per cent Al₂O₃ content at 1300°C, and the slag composition has been condensed so that ZnO + CaO + SiO₂ + FeO equals 100 per cent. Isobars have been constructed for constant ZnO activity, and are shown as dotted lines. It is clear that the activity coefficient largely depends on the CaO/SiO₂ ratio and increases as the ratio increases.

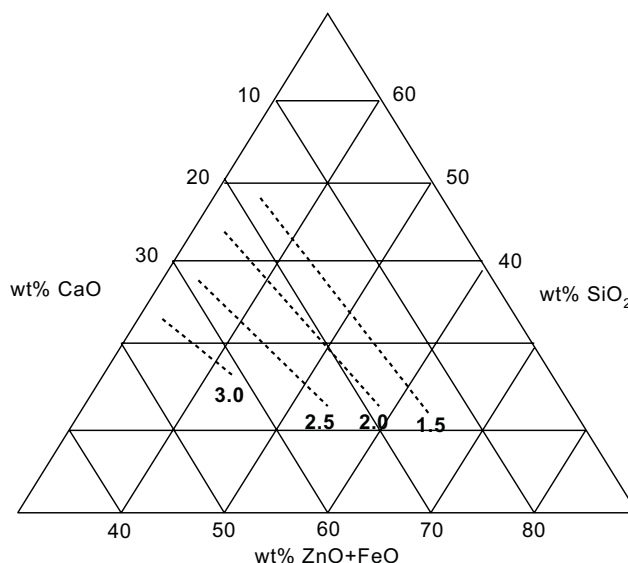


FIG 11.6 - Activity coefficient for zinc oxide in slag at 1300°C.

At a fixed CaO/SiO₂ ratio the activity coefficient also increases as the Al₂O₃ content is increased. For example, a typical lead blast furnace slag may have an activity coefficient of 2.0 at 8.5 per cent Al₂O₃, and this will increase to around 2.5 at 22.5 per cent Al₂O₃.

As indicated above, there has been conjecture about the principal mechanism for reduction from a molten phase and whether the process is in chemical equilibrium or is controlled by reaction kinetics and mass transfer. Initial studies of the reduction reactions in slag fuming (Bell, Turner and Peters 1955; and Kellogg, 1957) assumed that reaction rates were sufficiently high at operating temperatures above 1000°C for equilibrium conditions to prevail. Kellogg (1967) developed a mathematical model of the slag fuming process on this basis, and this was subsequently further developed and applied successfully at Port Pirie (Grant and Barnett, 1975) and at Boliden (Bygden *et al*, 1985).

Empirical models were also developed for fuming processes, indicating an approach to a first order reaction with respect to zinc concentration in the slag (Quarm, 1968). Application of the models developed for one operation did not necessarily apply to another and slag properties such as viscosity clearly had a significant influence. Some operations more closely followed a zero order reaction in which the zinc reduction rate was independent of the zinc concentration in the slag, at least above a level of around four per cent zinc in slag (Richards, Brimacombe and Toop, 1985). Richards *et al* (1985) indicated that solid carbon within the melt was significant, and the kinetics of the process may be controlled by the injection of coal particles into the slag bath as opposed to retention as a suspension in the gas phase. The kinetics can therefore be enhanced by high velocity injection.

The rate of reduction of zinc oxide in slag is also influenced by the FeO and sulfur contents of the slag. Rates are progressively increased as the FeO content increases. This is attributed to the reduction of zinc oxide by ferrous iron and the subsequent reduction of the ferric iron formed by CO. FeO thus acts as a catalyst for the reduction reactions. Rates are also reduced by the presence of sulfur in the slag, thought to be caused by surface blockage of the gas – slag interface due to the surface active nature of sulfur in the slag (Dal and Rankin, 1993).

There are clearly a number of parallel reduction reactions and it would appear that their predominance depends on physical conditions and the operating conditions of the furnace. Some reactions may have low resistance and are not rate limiting, and others, such as those involving solid carbon in the melt, are kinetically controlled and can be enhanced by giving attention to carbon particle sizing and injection methods. Slag properties, particularly viscosity, can have a bearing on the kinetics and can also change as the zinc concentration is depleted. However, it is now accepted that, with an adequately deep slag bath limiting the opportunity for gas by-passing, equilibrium is essentially achieved so that the Kellogg model can be applied (Ward, 2000).

In most practical slag reduction operations, coal is used as the source of carbon. Hydrocarbons are present and hydrogen can be formed giving rise to water vapour in reduction gases, which can result in re-oxidation of zinc vapour as the temperature is lowered. This will make condensation of zinc from reduction gases difficult but is not a disadvantage for fuming operations producing ZnO. Natural gas should therefore be a suitable fuel, but it was found that reduction rates fell significantly when coal was replaced by natural gas. In work at the Chinkent Lead Smelter-Russia (Izbakhanov *et al*, 1990), this was attributed to the slow decomposition of the hydrocarbons, which then tended to pass through the molten slag and burn above it. Oxygen potential in the injected gas was therefore high and tended to oxidise iron in the slag to magnetite. This precipitated as a solid phase and raised the viscosity of the slag, further reducing reduction rates, or in the extreme causing the bath to freeze. Cracking and pre-combustion of the natural gas to CO before injection into the slag bath overcame most of these difficulties.

Processes utilising molten phase reduction usually employ *in situ* combustion of fuel to maintain operating temperature and to provide the necessary heat to balance endothermic reduction reactions and heat loss through the furnace walls. The gas phase is thus further diluted with nitrogen as well as having high levels of CO₂ for maximum fuel utilisation efficiency. The thermal efficiency of the process can be improved by preheating input air to reduce the combustion fuel required and by the use of oxygen enrichment to reduce the volume of gas to be heated. However, the flow of gas does serve to enhance the removal of zinc vapour from the bath and there are limits to the positive impact of oxygen enrichment.

CONTROL OF IRON REDUCTION

One of the issues in many processes for the reduction of zinc oxide from slags is the control or avoidance of the formation of metallic iron. Iron has a wide melting range depending on the carbon content. The minimum liquidus temperature of 1130°C corresponds with a eutectic at 4.3 per cent

carbon. This rises to 1535°C for pure iron with no carbon content. For carbon contents above 4.3 per cent the liquidus temperature again rises. From usual reduction processes it would appear that the carbon content of iron formed can be around three per cent, melting at 1250°C. If the iron is decarburised by moving to reaction zones of higher oxygen potential, it can freeze and cause severe accretion problems. Therefore, operating conditions are often selected to avoid or minimise the formation of metallic iron.

Iron formation results from the reaction given in Equation 11.21:



Based on the thermodynamic data given in Appendix 1 and the principles used for the development of similar data for zinc oxide reduction (Equation 11.12), the Standard Gibbs Free Energy for Equation 11.21 can be given as Equation 11.22:

$$\Delta G_{21} = -792 + 1.905T - 0.1252T \ln T - 0.000471T^2 + 1.334 \times 10^{-7}T^3 \quad (11.22)$$

Using Equation 11.6, the equilibrium constant for the reaction 11.21 can be calculated as in Equation 11.23:

$$K_{21} = \frac{p_{\text{CO}_2} \cdot a_{\text{Fe}}}{p_{\text{CO}} \cdot a_{\text{FeO}}} = \exp\left(-\frac{\Delta G_{21}}{R \cdot T}\right) \quad (11.23)$$

where:

a_{Fe} is the activity of the iron formed taken as 1.0

a_{FeO} is the activity of FeO dissolved in the slag.

The activity of FeO in ternary system slags is shown in Figure 11.7, from which it can be deduced that typical slags of around 35 per cent FeO will have an activity of around 0.4.

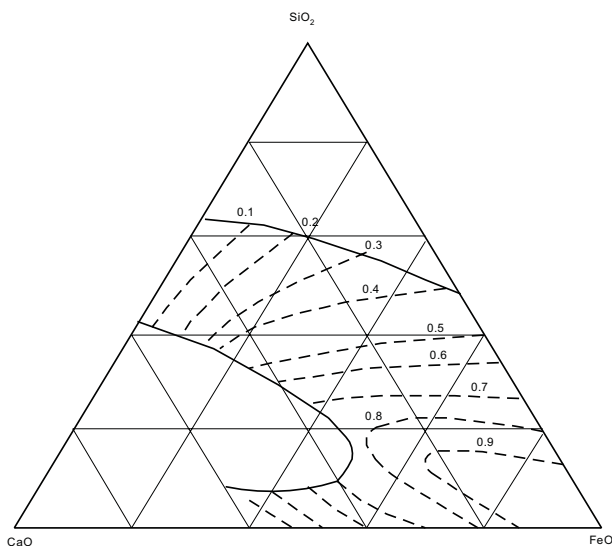


FIG 11.7 - Activities of FeO in system FeO-CaO-SiO₂ at 1600°C (Elliot *et al*, 1963).

The competing reduction of ZnO and FeO can be illustrated by the equilibrium ratios of CO:CO₂ as a function of the temperature at which reduction occurs. These equilibrium curves are shown in Figure 11.8 for zinc at levels in a typical slag of 2.5 per cent and seven per cent, and for iron reduction at FeO levels in slag of 15 per cent and 45 per cent. Reduction will occur for CO:CO₂ partial pressure ratios in regions above the equilibrium curves. For regions above all curves, both ZnO and FeO will be reduced and iron will be formed. For regions at high temperatures above the zinc equilibrium curves and below the iron curves, ZnO will be reduced without the formation of metallic iron. Raising the zinc content or lowering the iron content will extend this region of no iron formation to lower operating temperatures. At low temperatures FeO will be reduced in preference to ZnO.

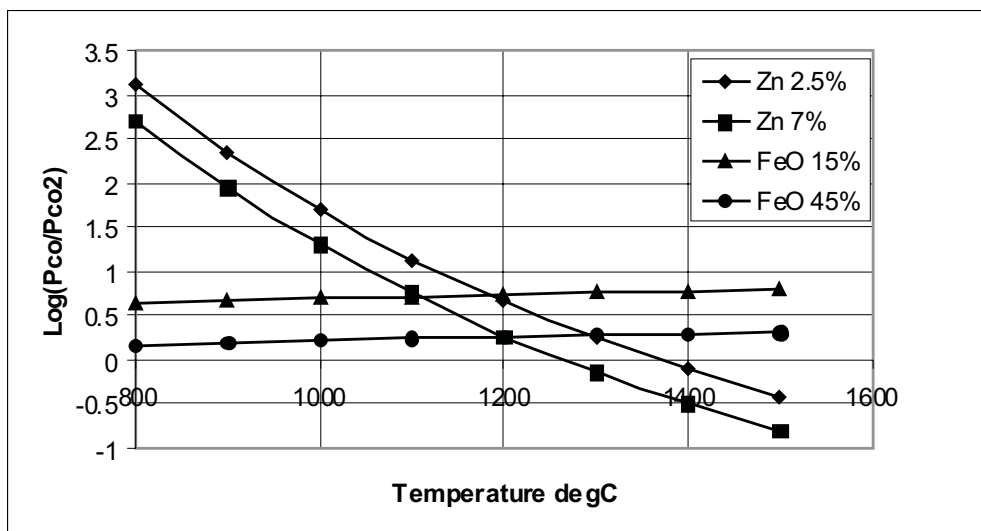


FIG 11.8 - Equilibrium curves for ZnO and FeO reduction.

For typical situations with slags containing around 35 per cent FeO, zinc can be fumed to levels of 2.5 per cent in final slag without iron formation if the temperature is above about 1250°C. For higher iron slags, such as the typical ISF slag, this temperature must be above 1300°C or if the slag contains seven per cent zinc, above 1200°C.

It should be noted that iron formation can enhance the formation of speiss, which if dispersed in the slag will make the slag an environmental liability for storage due to the potential leaching of arsenic.

CONDENSATION OF ZINC FROM REDUCTION GASES

For a carbothermic retort process operating at 1000°C and 1 atm total pressure, the partial pressure of zinc vapour is close to 0.5 atm. The dew point of zinc (the temperature at which liquid zinc first forms from the vapour) may be calculated from Equation 11.14 as 1115°K or 842°C. The condenser needs to operate well below this temperature to achieve sufficient condensation. Vent gases from the condenser will contain zinc vapour in equilibrium with the molten zinc formed at the operating temperature of the condenser, and will constitute a loss.

As the retort gases are cooled, the equilibrium will shift back to the left of Equation 11.1 and in effect any CO₂ present will re-oxidise the zinc to ZnO. This formation of ZnO also represents a condensation loss. At low temperatures it is also possible for CO to re-oxidise zinc vapour and form elemental carbon, but the reaction rates for this are relatively low and there is minimal carbon formation in a practical condenser system.

Theoretical condensation efficiency, as determined by the two losses due to oxidation by CO_2 and residual zinc vapour contained in vent gases, is shown in Table 11.2 for a carbothermic retort gas produced at 1000°C and 1 atm total pressure, and with the composition indicated above. Clearly it is important to operate the condenser at a temperature below 650°C .

TABLE 11.2
Theoretical zinc condenser efficiency (carbothermic retort).

Condenser Temperature $^\circ\text{C}$	Zinc loss by oxidation %	Zinc loss in exit gas %	Theoretical condenser efficiency %
500	0.34	0.007	99.65
550	0.34	0.04	99.62
600	0.34	0.18	99.48
650	0.33	0.7	98.97
700	0.31	2.34	97.35
750	0.26	6.92	92.82
800	0.12	18.4	81.48

In practice, the formation of zinc oxide from vapour phase re-oxidation of zinc results in the formation of droplets of molten zinc coated with oxide. The surface coating tends to prevent coalescence into the bulk of the molten zinc formed and results in the production of a powdered material within the condenser, termed 'blue powder'. The loss of zinc in blue powder can thus be significantly higher than the actual degree of oxidation indicated above. However, the actual degree of oxidation may be lower than the theoretical level indicated in Table 11.2 if the gas is cooled rapidly such that re-oxidation rates are reduced and the condensation rate is increased.

The carbothermic retort system with excess carbon present has the advantage that the equilibrium levels of CO_2 are low at high retort temperatures and the potential to re-oxidise zinc vapour on cooling the gases is also low. For other systems with greater levels of CO_2 present, this can be achieved by contacting hot retort gases with carbon to achieve an equilibrium shift to low levels of CO_2 .

In the case of hydrogen reduction, water vapour is the only reaction product and can completely and rapidly re-oxidise zinc vapour as the gas is cooled. Similarly, gases from the ISF contain sufficient CO_2 to re-oxidise all the zinc vapour present in the furnace gases. In the latter case, use must be made of the concept of rapid cooling of the gases and rapid condensation to lower oxidation rates and minimise the degree of re-oxidation. This practice is effective in reducing re-oxidation due to CO_2 but is not as effective for reducing re-oxidation due to water vapour.

Condenser systems have developed from the simple cooled attachment to a horizontal retort to systems designed to achieve quenching or rapid cooling of gases. The first commercially successful type of rapid cooling condenser was the zinc splash condenser as applied to the Vertical Retort by the New Jersey Zinc Company (see Figure 11.9). In this case, a rotating graphite impeller dipping into a molten zinc bath contained within the condenser chamber sprays zinc droplets into the gas stream, both cooling the gas and providing a surface on which zinc vapour can condense. The zinc bath is circulated through a cooling system to maintain a temperature below 550°C .

In the Weaton-Najarian condenser developed for the electrothermic retort, as shown in Figure 11.10, retort gases are bubbled through a molten zinc bath contained in a U tube arrangement to provide a seal. Zinc vapour is condensed as the gas bubbles through the molten zinc. This type of condenser is only useful if the gas flow is small with minimal inert components. Hence, it is generally only suitable for processes using electrical energy for heating. The bubbling action of the gas provides sufficient hydraulic head to circulate zinc through an external cooler without the need for pumps.

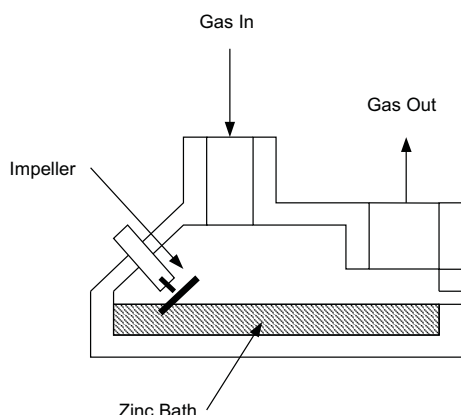


FIG 11.9 - Schematic of the zinc splash condenser.

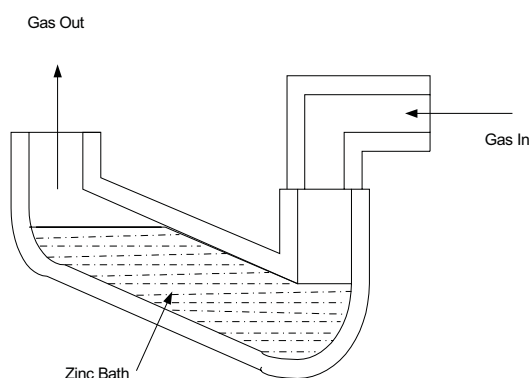


FIG 11.10 - Weaton-Najarian condenser (electrothermic retort).

To enable the handling of large volumes of gas with a relatively low zinc content from the blast furnace, the lead splash condenser was developed by the Imperial Smelting Company in the UK (see Figure 11.11).

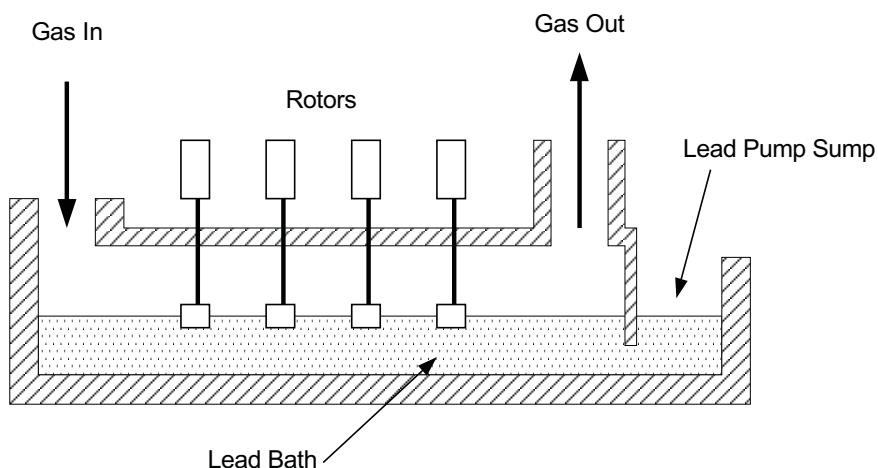


FIG 11.11 - Schematic of the ISP lead splash condenser.

The benefit of using lead was that zinc was sufficiently soluble in the lead at the operating temperature of the condenser of 550°C and provided an absorption action rather than simple condensation on the lead surface. The spray impellers could also be made of steel instead of graphite as required for a molten zinc system. This provides a better opportunity for design of the impeller to give optimum spray generation with more control over the droplet size as well as the volume of lead lifted. The mutual solubilities of zinc in lead and lead in zinc are shown in Table 11.3 and indicated that lead at 550°C will dissolve about four per cent zinc. As the lead is cooled to around 450°C , the solubility drops to around two per cent, allowing zinc to separate and float to the top of the lead stream, which is then recirculated to the condenser. That zinc will contain around 1.4 per cent lead. On this basis, about 50 tonnes of lead need to be circulated to collect one tonne of zinc.

TABLE 11.3
Mutual solubilities of zinc and lead.

Temperature °C	% Zn in Pb	% Pb in Zn
318.2	0.5	
400	1.5	
417.8		0.9
450	2.1	1.4
500	3.0	2.3
550	4.2	4.0
600	5.9	5.9
650	8.0	9.0
700	12.0	15.0

Rapid cooling of gases containing zinc vapour can cause excessive nucleation of zinc particles and the formation of a fog, defined as zinc droplets with a size much less than one micron. These droplets are difficult to capture and condense once formed, and act as nuclei for any oxidation products, thus forming 'blue powder'. Capture of fine droplets is aided by maximising the surface area of the lead spray and by the generation of small lead droplets by the spray impellers. Hence, the design and positioning of the impellers is most important. Collection efficiency is also improved if the gas passes through a number of sprays in series, and the Imperial Smelting lead splash condenser usually has four stages in series. With a collection efficiency of say 50 per cent of the zinc in vapour passing each stage, the theoretical efficiency for four stages in series will be around 94 per cent.

Dross formed within the condenser and collected on the surface of the lead bath interferes with the action of the impellers and can significantly decrease the efficiency of the condenser. Dross is formed from dusts carried over from the reduction process, from re-oxidation of zinc as the temperature is lowered, and from halides and other volatile compounds, which can also condense as the gas is cooled.

Table 11.4 gives the vapour pressure-temperature relationships for various volatile compounds that can be present in gases from reduction processes and have potential to form condenser drosses or be collected with the molten zinc. For compounds with appreciable vapour pressures at reduction

TABLE 11.4
Temperature-vapour pressure for volatile compounds.

Vapour pressure (mmHg)	20	400	760
Compounds	Temperature at given Vap Pressure (C)		
FeCl ₃	246	298	319
Cd metal	516	711	765
ZnCl ₂	536	689	732
Zn metal	632	844	907
PbCl ₂	684	893	954
FeCl ₂	737	961	1026
PbS	1005	1221	1281
KCl	1020	1322	1407
NaCl	1072	1379	1465
PbO	1134	1402	1472
Pb	1234	1630	1744
ZnO	1450		
ZnS	1580		

temperature of around 1200°C (zinc, lead and iron chlorides) and a vapour pressure at condensation temperature (550°C) lower than their content in the gas stream, there will be potential to condense and form a dross. As well as forming surface drosses on the lead bath, these materials can also condense on the inner surfaces of the condenser forming sticky accretions, which can rapidly build to the point where shut down and cleaning is necessary.

The condenser inefficiencies associated with dross formation were a primary cause for the failure of a number of processes developed during the 1990s for the treatment of steel plant dusts and involving direct reduction to zinc metal. In particular, high levels of iron (both metallic and oxides) carried over in dusts as well as halides gave rise to heavy accretion formation, which was difficult to remove.

Vent gases from a practical condenser system, containing residual zinc vapour and 'blue powder' are usually processed in a scrubber where the zinc is oxidised and is recovered for recycle. The recycle of oxides, blue powder and drosses to the reduction process can build up circulating loads, particularly of halides unless alternative outlets are provided. However, if the amounts are relatively small, these recycles do not represent losses in overall process recovery, but represent losses in first pass recovery.

FUMING

Where reduction processes are treating low-grade materials and producing gases containing low levels of zinc vapour and a large proportion of combustion products such as CO₂ and H₂O, it is impractical to consider condensation to liquid zinc and it may be preferable to allow the zinc vapour to be oxidised to ZnO. Similarly, if the gas contains high levels of dross forming compounds such as dusts and halides, direct condensation can be impractical and oxidation to zinc oxide is necessary. The zinc oxide so formed is generally of submicron size and is termed a fume. It may be collected by cooling and filtering or scrubbing the resulting gas stream. The oxidation of zinc in the vapour phase will generate heat and in some fuming processes this heat can be partly recovered to reduce heat requirements for the reduction stage. Otherwise it can be recovered as steam.

Fuming processes offer considerably greater flexibility in terms of fuel use and the application of *in situ* combustion, since gas composition is not a critical issue as is the case where condensation is required. These processes provide a means of recovering zinc in a concentrated form from low-grade waste materials and residues, and include slag bath fuming processes and the Waelz kiln process. Fuming processes are detailed in Chapter 16.

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Sintering

PURPOSE AND BACKGROUND

The purpose of sintering is to roast material at sufficient temperature to cause partial melting so as to form a porous cake of sufficient cohesion and strength to be suitable as feed to a carbothermic reduction process, such as retorting or a shaft furnace. It can also be used to eliminate sulfur from feed materials, in which case sulfides can form the fuel for the operation, otherwise coke fines are commonly used.

Sintering was first developed for the preparation of lead sulfide concentrates for blast furnace smelting. It was initially applied to zinc for the preparation of feed for horizontal retorts from zinc sulfide concentrates and later for vertical and electrothermic retorts. Extension to the preparation of feed for the zinc blast furnace imposed more demanding controls and performance of the sintering process in order to produce suitable quality sinter. It is for this purpose that zinc sintering operations are largely used today.

THE SINTERING PROCESS

Sinter quality is of key importance for subsequent processing, but is difficult to define and measure in quantitative terms, as the ultimate measure is essentially optimum performance of the blast furnace or alternative reduction process. Sinter must be strong and coherent to withstand handling without significant degradation and breakage. It should be reasonably porous to allow gas-solid reduction reactions to take place to the maximum extent, and it should have a suitably high melting temperature or softening range in order to maintain its structure and integrity for the maximum possible time during the reduction process. For the reduction processes in which sinter is used, relatively low sulfur contents are also important.

Sintering was first developed as a batch pot roasting technique using a crucible fitted with a grid base through which air could be blown. Coal was first ignited on the base then sulfide materials were progressively added and burned until the crucible was full. It was then emptied and the process repeated. This approach was soon mechanised with the development of the Dwight Lloyd sinter machine based on the principles of the chain grate stoker used for coal fired boilers. It consisted of an endless looped chain of steel pallets, each made from a frame fitted with steel bars to form a grate. Material to be sintered was placed on the grate which then moved under a gas or oil fired ignition stove to heat and ignite the top layer. Air was drawn through the charge using a series of suction wind boxes located beneath the pallet chain and sealed by side plates attached to each pallet. As the grate slowly moved forward, the combustion zone moved downward through the material until combustion was completed. At the end of the machine, air passing through the sintered material served to cool the sinter before it was discharged. The pallets moved over guides at the discharge end of the machine and returned beneath the wind boxes to the feed end.

The time required for sintering a bed of up to 400 mm deep is usually around 30 minutes, which represents the speed of one pallet traverse from the position of ignition to the discharge end or 'tip end' of the machine. The process may be considered in terms of a number of zones moving through the charge bed as illustrated in Figure 12.1.

In the top zone, sinter already formed is cooled by incoming air and the air is heated. Hot air then passes through the reaction zone where combustion of the fuel occurs with some degree of melting. In the third zone hot combustion gases heat the unburned charge up to ignition temperature and the gases are progressively cooled and pass to the fourth zone where drying of the material takes place and gases are further cooled and humidified.

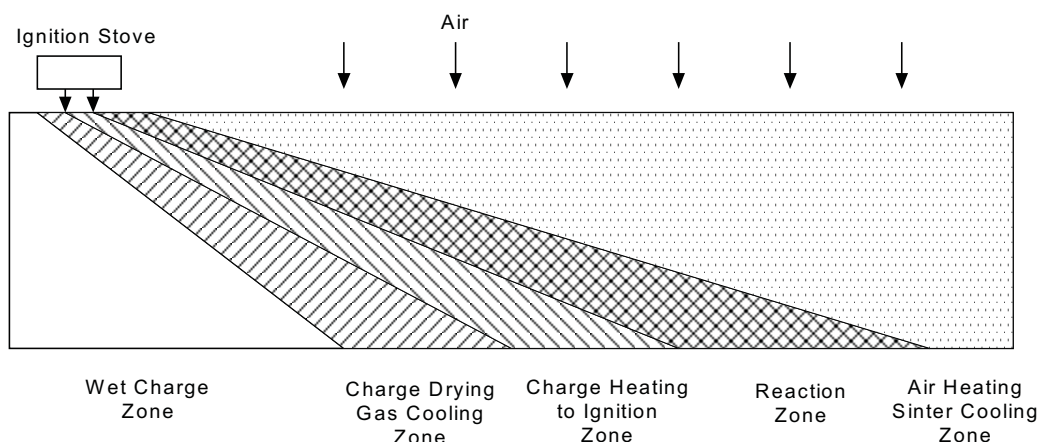


FIG 12.1 - Separate zones in the sinter charge bed – downdraught conditions.

The temperature profile of a point within the bed as a function of time (or position along the machine) is illustrated in Figure 12.2.

The peak bed temperature is an important parameter for the formation of sinter with the required properties. The uniformity of attainment of this condition throughout the sinter bed is critical. In order that this uniformity is achieved there must be constant conditions for the combustion reactions. This in turn requires close attention to the sulfur or fuel content of the charge. Uniformity in the blending of charge components as well as sizing and packing uniformity of the bed to allow for even air flow and oxygen access is also required. A number of operating parameters need to be closely controlled to achieve this, as discussed below.

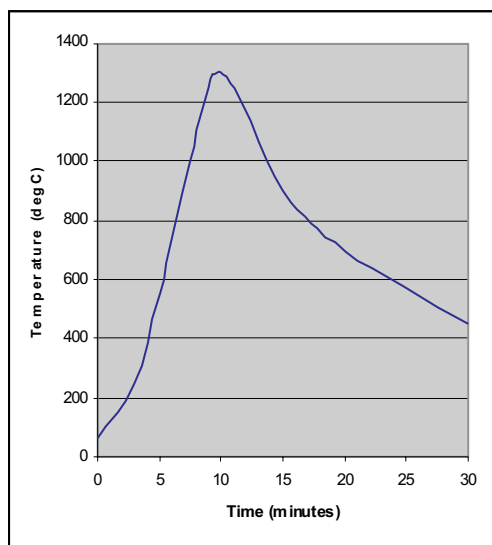


FIG 12.2 - Typical sinter bed temperature profile.

Gas permeability of the bed during the sintering process is important. Permeability can be reduced by the effect of moisture evaporation from the charge and recondensation in the colder downstream layers of the bed. More importantly, permeability can be reduced by entrainment of fine particles on drying causing blockage of the bed by collection and concentration of these fines in the downstream layers, aggravated by the collection of excess moisture. To avoid this, some form of binding of fine concentrate particles to the return sinter is needed and often the addition of a small amount of CaO will serve this purpose. Otherwise, the presence of soluble salts such as zinc sulfate in the moisture content of the sinter can be beneficial. In addition, excessive melting and formation of liquid phases can also cause a reduction in bed permeability. However, a sinter comprised of excessive amounts of low melting point phases sufficient to cause this, is not likely to be of acceptable quality, and needs to be avoided in any event.

Fuel Content of the Sinter Charge

In practice for the sintering of zinc sulfide concentrates, a sulfide content of the charge of around six per cent is required to achieve the necessary peak bed temperature. Since concentrates are normally around 30 per cent sulfur they must either be diluted considerably or partially roasted before sintering. Partial roasting has commonly been used for retorting process feed preparation or a mix of dead roasted and fresh concentrates. However, for blast furnace processing of sinter, dilution with recycled sinter is the preferred approach because of the high degree of control over particle sizing that can be achieved. A dilution ratio of five times is required for a sinter recycle, fresh feed ratios of the order of 4:1 depending on fluxing needs and other inert recycle materials added to the sinter charge. Coke fines can also be used as a fuel or as a fuel supplement.

Different sulfide mineralisation can exhibit different ignition temperatures and combustion rates. Optimum conditions may be achieved by specifying certain levels of particular components in a sinter charge to aid ignition or attainment of peak bed temperature, and to complete combustion within a given time or position on the sinter machine. The presence of galena in the preparation of ISF sinter is important for ignition, and minimum levels in the charge can be specified.

Charge Mix

Because of the high degree of compositional uniformity required, controlled proportioning and mixing of all feed components is critical. This includes weigh feeding and controlled blending of a number of concentrate feeds as well as fluxing materials, recycle fumes and residues, and return sinter. For this purpose, the plant usually includes a feed blending and proportioning facility made up of a series of storage silos for each component, each fitted with weigh feeders and discharging onto a common collection conveyor that feeds the primary mixer.

Another method used for blending of feed materials is the use of 'bedding' or the building of a heap made up of layers of component materials on the floor of a storage building. The material is then reclaimed by fully excavating the face of the heap, thus producing a blend in the same proportions as the heap was constructed. This method is inflexible in that the blend cannot be varied once the heap has been constructed, unless trimming additions of mix components can be made after reclamation.

Sizing of the Charge and Moisture Content

In order to have sufficient uniform flow of air through the sinter bed, there needs to be a uniformly sized porous bed, with a reasonably coarse average particle size. Since concentrates are usually quite fine, the sizing of the charge will largely be determined by the sizing of the return sinter representing the bulk of the charge, and the degree of agglomeration achieved in feed preparation. The ideal situation is to have uniformly sized and relatively coarse particles of return sinter coated with a layer of fine concentrates, thus forming an open structure with the concentrates exposed to the air flow to the maximum extent. To meet this condition, return sinter is crushed using crushing rolls to a particle size of less than 5 mm. Moisture is added to the charge to assist in binding the concentrate particles to the surface of the sinter. The total charge is mixed in a pug mill and tumbled in a drum to achieve the coating action and some degree of pelletisation. Disc pelletisers have been used in place of a drum, but generally the residence time is too short for efficient final mixing and product uniformity.

The level of moisture is quite critical for the mixing and preparation operation, and is usually between six and seven per cent. Too much moisture will physically reduce porosity and permeability of the bed, whereas too little will not give the degree of uniformity of coating of the sinter particles and hence uniformity of the particle sizing of the bed. Inadequate moisture addition will also cause a reduction in bed permeability. This is due to the lack of attachment of fines to the coarser particles and

their tendency to move and block gas passage through the bed. Measurement of the moisture content of sinter feed with feed-back to water additions at various mixing points is thus an essential part of good sinter machine control.

Machine Feeding

Even laying of the charge across the width of the sinter machine grate is critical in avoiding variable permeability and uneven air flow through the bed. A reciprocating conveyor or swing chute are commonly used to evenly fill an open hopper located above the grate. The gap between the grate and the base of the hopper sets the depth of the bed and can be adjusted using a sliding plate. The width of the gap in relation to the width of the hopper can also influence the packing density of the bed and needs to be carefully evaluated. Variations in the depth of material held in the hopper can impact to some degree on the packing density and it is preferable to maintain the hopper at a constant level. This can be done by varying the machine speed for a given feed rate or by varying the feed rate to the hopper for a set machine speed. The latter control is probably preferable but is more complex since feedback control to all components of the feed preparation chain will be necessary. However, since this represents a fine balancing control it is more usual to set a feed rate and vary machine speed as a balancing control.

Gas Distribution

In general, the combustion of most of the sulfur tends to take place towards the feed end of the sinter machine, and the concentration of SO_2 in gas is much lower towards the 'tip end' of the machine. A typical gas concentration profile is shown in Figure 12.3 for a machine with ten windboxes.

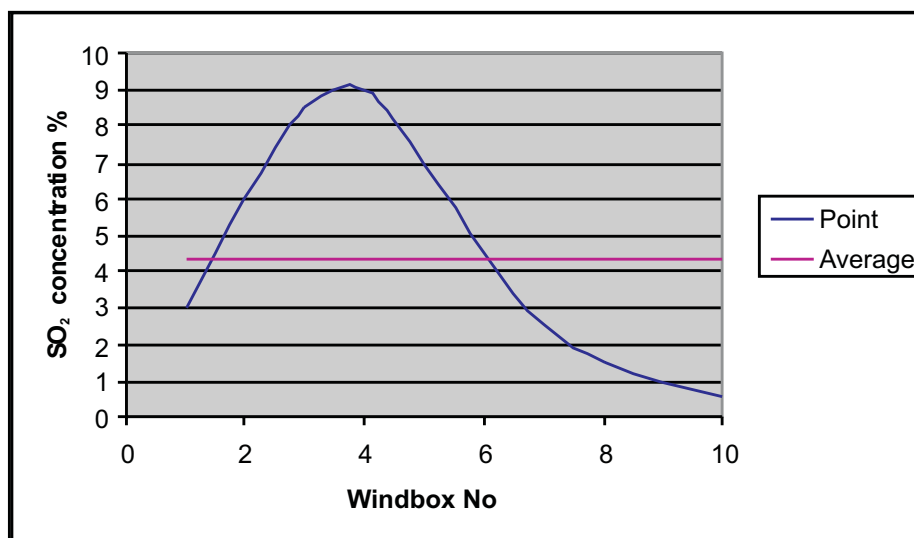


FIG 12.3 - Typical sinter gas composition profile.

Since there is considerable excess oxygen in the gas stream it is common practice to recirculate gas from the tip end of the machine back into the front end in order to reduce the volume of sinter gas and raise the average SO_2 concentration from 4.5 per cent to around six or seven per cent so that it is suitable for sulfuric acid production. Otherwise it has been the practice to collect only part of the gas from the feed end for acid production and discharge the tail end gas to atmosphere. However that practice is less acceptable today, and tip end gas recirculation is now an important requirement for environmental control.

UPDRAUGHT SINTERING

The initial development of sintering was based on the principles described above, wherein air passes down through the sinter bed to windboxes located beneath the sinter machine grate and under suction – so termed ‘downdraught sintering’.

The downdraught action tends to compress the bed against the grate and reduce permeability as well as tending to lodge particles in the grate openings causing blockages. It was also found that in lead sintering or where significant levels of lead are present, metallic lead tends to form in the sinter and drain down onto the grate where it can freeze but more particularly cause severe corrosion of the grate bars.

These problems can be overcome to a large extent by blowing air upwards from pressurised windboxes and collecting sinter gas from a hood covering the machine. The updraught sinter machine has improved productivity and is now the most commonly used design. All sintering plants associated with the Imperial Smelting Furnace use updraught sintering and a typical flow sheet is given in Figure 12.4.

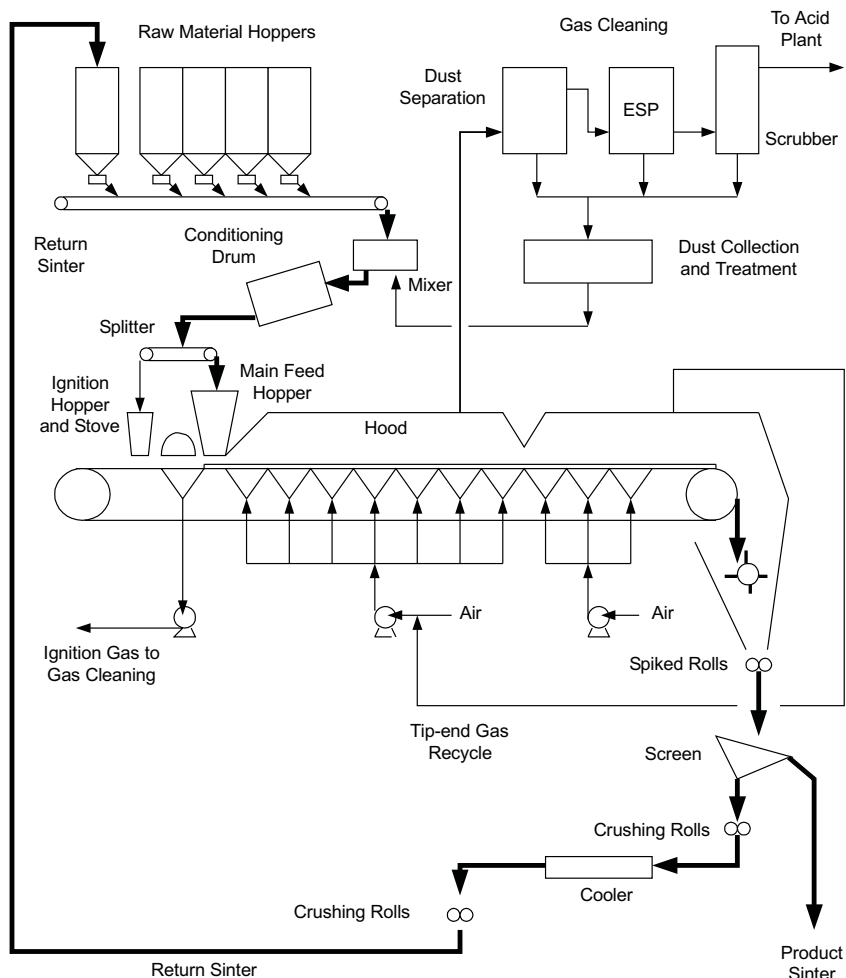


FIG 12.4 - Flow sheet of an updraught sintering machine.

Ignition of the charge is still by downdraught on a shallow layer of around 30 mm laid on the grate ahead of the ignition stove. After ignition of that layer the full charge depth of 300 to 400 mm is placed on top of the ignited layer and air flow is reversed to updraught for the remainder of the machine. The combustion zone moves upwards through the charge and breaks through the upper surface at around 80 per cent of the machine length.

Feeding the machine is then in two parts – one position for the ignition layer and one for the main layer. In some machines entirely separate feed systems are used, in others the feed is split to the ignition hopper and the main hopper using an intermittent diversion chute or conveyor. The disadvantage of the latter system is that the level in the hoppers varies and as indicated above can vary the packing density of the sinter charge. It also makes smooth control of the machine more difficult if controls are linked to the level of material in the main feed hopper.

SINTER HANDLING

Sinter breaks away and falls from the tip end of the machine in large slabs that fall through breaker bars and a set of spiked rolls to break the sinter into lumps, which are then separated using a 25 mm screen. Oversize represents product sinter suitable for feed to the blast furnace or reduction process. Undersize is cooled through a drum or cooler conveyor and is then crushed using two sets of rolls in series. The final rolls are normally set at around five to 6 mm. The resulting crushed sinter constitutes return material and is sent via a surge bin to the feed mixing facility. Control of the gap in the final rolls crusher is quite critical to the sizing of the return sinter and to the performance of the process and the production of quality sinter. These rolls tend to wear unevenly and give rise to a variable gap width and hence a wider size distribution of crushed sinter than is desirable. Hence regular maintenance and re-machining of the rolls surfaces is necessary.

Coarse product sinter from the primary screen is sent directly to surge bins feeding the reduction process and often material drawn from these bins is re-screened to remove fines, which are also recycled as return sinter to the feed mixing section. Provision is made to crush and return product sinter to make up the required recycle ratio. Under steady state operation of the sinter machine, control of the amount of product sinter returned is normally through the level of material in the returns sinter surge bin, which is drawn off at a steady rate to satisfy feed blend requirements.

Severe imbalances and instability of the process can result from the production of poor quality sinter. Friable sinter of low strength gives excessive fines, which can exceed the requirements for recycle. In such a situation recycle sizing can be reduced, sending more fine material to product, which can have a detrimental effect on blast furnace operation. Finer sizing of the returns sinter can also affect sinter machine performance by restricting the permeability of the sinter bed, and can possibly perpetuate the problem. This situation can particularly arise on machine start-up and it is often preferable to discard poor quality material to stockpile for later slow reclamation as returns. The problem can also arise with departure from critical controls such as moisture content of the feed, sizing and feed blending controls, and can lead to process instability and difficulty in restoring product sinter quality. A disturbance will recycle with the returns cycle time, which can be measured in hours. It may dampen with time (requiring many hours), but in extreme cases can increase out of control, necessitating rejection from circuit to restore stable operation. In this regard, the sintering process is inherently unstable and is a particularly difficult process with a high degree of intolerance to departure from stable operating conditions.

GAS HANDLING AND CLEANING

The net gas output from the sinter machine is at a temperature of around 500°C and is cleaned by drop out of dust in an open chamber or flue, followed by hot electrostatic precipitators and gas scrubbing. Collected dusts generally amount to two per cent of the input sinter charge and contain relatively high levels of lead and cadmium, and sometimes other volatile elements such as selenium and mercury.

Mercury generally remains in the gas and must be removed by scrubbing prior to the production of sulfuric acid. Collected dusts may be directly recycled to the sinter plant feed, but usually there is benefit in extracting highly volatile elements that would otherwise build-up circulating loads. Cadmium is a particular case in point and can be removed from collected dusts by acid leaching. If not removed, the cadmium reports totally to final product zinc and increases the load on the refining stage.

After leaching, the dusts are filtered and the filter cake is returned to the sinter feed mixer. This cake will add significant levels of water and careful control is necessary. After cleaning by scrubbing, the gas is passed to a standard contact sulfuric plant.

THE STRUCTURE OF SINTER

In order to perform in a shaft furnace or other carbothermic reduction processes, sinter must retain its physical structure for as long as possible before melting and forming slag. Zinc oxide reduction rates are highest from gas-solid reactions and lowest from the liquid slag. If the sinter softens and becomes a sticky mass it can restrict access of reduction gases to ZnO surfaces and can in extreme cases, plug the furnace and restrict the flow of both the charge and gas. The key parameter is therefore the melting temperature or the softening temperature range of the sinter. This is very much a function of the mineralogical composition and structure of the sinter. The structure may simplistically be considered as a matrix of crystalline phases cemented together by a glassy phase usually composed of CaO-PbO-SiO_2 . The crystalline phases include zincite (ZnO) and franklinite (ZnFe_2O_4). Good sinter contains zincite as long needle crystals rather than rounded grains. This structure develops only at high temperature and it is important that peak bed temperature during sintering is around 1300°C for this to occur. Such a structure does not develop below 1200°C .

Other crystal phases that provide structural support to the sinter have been recognised as important, such as Melilite, which is a complex mixture of calcium and aluminium silicates containing zinc, iron and magnesium.

The relative amount and melting temperature of the glassy phase or phases are also critical in terms of determining the softening of the sinter structure. For instance, lead silicates have low melting points in the range of 600 to 800°C depending on composition. Melting points can be raised by the addition of CaO to increase the CaO:SiO_2 ratio and a level above 1.6:1 is generally preferable. The addition of CaO usually raises the temperature at which softening commences as well as reducing the temperature range between initial softening and the molten state. This effect is due to the decrease in the volume fraction of lead silicate phases with a wide softening range.

It is also important to have sufficient iron present to form a calcium ferrite eutectic, which can replace franklinite and displace zinc to form zincite (ZnO). The eutectic forms a glassy phase with a melting point above 1200°C .

The microstructure of sinter can be quite complex where low grade feed concentrates are processed and there is a significant level of gangue minerals present. However, consideration of the details generally points to the need for high peak bed temperatures during sintering to promote crystallisation, and to the need for correct fluxing in order to achieve the appropriate matrix composition as well as the ultimate process slag composition (Holliday, Shoobridge and Firkin, 1980).

SINTER MACHINE CAPACITY AND PERFORMANCE

In general, the sintering process involves a large number of variables and the formation of a material with a complex microstructure. It is a difficult process to control and is inherently unstable when subject to significant disturbances. Good performance thus tends to rely on a skilled and experienced workforce. The generation of poor quality sinter can have significant impact on the performance of the reduction processes that follow, particularly the blast furnace, and can greatly restrict its throughput.

Sinter machines vary largely in size ranging from small machines of 12 m² grate area up to 110 m² with a grate width of up to 3 m. Capacity is normally expressed in terms of the sulfur burning capacity and is in the range of one to two tonne/day per m² of grate area, with a typical figure of 1.7 t/day per m². For an ISF plant this would correspond to a net sinter production capacity of around seven tonne per day per m² of grate area. Details of some sinter machines associated with ISF smelters are given in Table 12.1.

TABLE 12.1
Commercial sinter machine capacities (ISFs).

Plant (See Table 1.4)	Grate area (m ²)	S burning rate (t/m ² /day)	Sinter prod (t / day)	SO ₂ in gas (%)
Hachinohe	90	1.78	670	7.0
Harima	70	1.63	550	6.3
Duisburg	72		550	6.2
Porto Vesme	70	2.2	600	6.3
Chanderiya	120	1.6	540	3.5-5.0
Cockle Creek	95	1.8	650	6.5

The use of oxygen enrichment of the air blast has been evaluated as a means of increasing machine capacity in terms of the sulfur elimination rate. This can be achieved, but since oxygen is used in large excess and hence inefficiently for sulfur combustion, enrichment is generally not economically justified.

One means of increasing the zinc throughput of a sinter machine is to use an oxidised zinc feed material as a sinter returns replacement. For this purpose, the material needs to be correctly sized and some form of agglomeration may be necessary, but it must be sufficiently strong to retain its form and size. Clinkered Waelz oxide is a suitable material for this purpose.

In general terms, sinter machine installations are complex with many moving parts, operating in a hot dusty environment and consequently are relatively high maintenance items. The high level of solids recycle and hence the total material handling loads per unit of output significantly adds to the costs of the process.

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Retorting Processes

HISTORICAL

Historic methods of zinc production were based on batch retorting methods in which calcined calamine ores (zinc carbonate) were mixed with charcoal and placed in clay crucibles. These were in turn placed in a furnace that heated the base of the retorts. The top of the crucible projected from the furnace and remained cool enough for the zinc vapour to condense. After a batch firing the crucibles were cooled and broken open to extract a mass of crude zinc metal from the cooler top section of the retort. Collected zinc was then melted and drossed to produce zinc metal or 'spelter' as it was termed.

The operations of William Champion at Warmley near Bristol in the UK (1743) improved on this procedure by fully enclosing the retorts in the heating furnace and adding a wrought iron exit pipe leading from the upper section of the retort out through the base of the retort and the furnace. The pipe acted as a zinc condenser and molten zinc would drip out from the pipe for collection in a water-filled pan.

Significant improvements were made by Johann Ruberg at Wessola in Upper Silesia, who designed the precursor to the horizontal retort in 1798. As shown in Figure 13.1, a series of horizontal retorts were packed with calamine and charcoal and were connected to an external condensing chamber to collect zinc as a liquid.

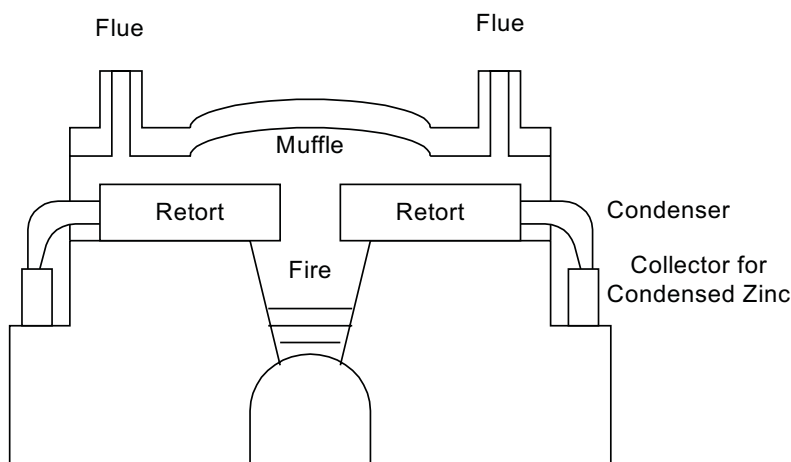


FIG 13.1 - Early silesian retorting process.

Further developments by Abbe Dony in Liege, Belgium in 1808 formed the basis of the horizontal retort process and was the principal method of zinc production for over one century up to the development of the electrolytic process in 1916.

THE HORIZONTAL RETORT PROCESS

Typical horizontal retort furnaces consisted of coal or producer gas fired furnace chambers containing four rows of retorts on each side, usually arranged in groups of 16, with up to 400 on each side of the one furnace chamber. A typical layout is shown in Figure 13.2. Furnace combustion gases circulate around the retorts heating them from the outside.

Retorts were made from clay and were typically 230 mm diameter and 1500 mm long with a wall thickness of around 25 mm. Life of a retort was around 20 cycles of 24 to 48 hours, requiring more than 1.2 retorts per tonne of zinc produced. As a consequence, production of retorts was an integral part of the operation. Individual condensers were usually attached to each retort. These were also manufactured from clay and were of simple conical form, 500 mm long and with a mouth diameter of around 70 mm. Condenser life was about one third of the life of the retorts and were either reused or replaced after each refilling cycle.

Both retorts and condensers were cured and fired to around 1100°C. New retorts were generally transferred hot from the firing kiln to the retorting furnace to minimise stressing of the retort when it is rapidly reheated.

Retorts were sealed into the furnace chamber using fireclay and the condensers were similarly attached.

Furnaces operated on a 24 or 48 hour distillation cycle. 24 hour cycles were the normal practice in Europe and 48 hour cycles in the USA where lower fuel costs favoured the longer cycle and gave marginally greater zinc recovery. At the end of the cycle the condensers were removed and set aside for reuse or for disposal. The contents of the retort were removed by a variety of devices such as mechanical scrapers or compressed air blowers, and were directed into a chute discharging into a hopper located below the face of the furnace. One issue was the formation and collection of a hard iron-rich slag on the walls of the retort, which tended to interfere with and slow the charging operation.

The charge mix consisted of sinter (at 60 to 70 per cent zinc content) and low volatile, low ash anthracite coal or coke fines. The weight of reductant was in the range of 25 to 35 per cent of the charge. A small amount of salt was normally added (two to three per cent) to act as a chloride flux, assisting condensation and reducing 'blue powder' formation. The sizing of sinter and carbon was generally between three and six millimetres for high gas permeability.

Charging of the retorts was originally a manual operation but many different designs of mechanical charging machines were developed using conveyors such as augurs or using blowers and slingers. After charging, cleaned or new condensers were fitted and fixed with fireclay. This required careful positioning with the bottom surface being horizontal. The condenser outlet was filled with a 'stuffing mixture' which dried to a porous barrier retaining molten zinc but allowing gases to escape. For tapping, the stuffing was broken and molten zinc flowed out into a collection ladle. For efficient removal of molten zinc it was important that the lower surface of the condenser was horizontal. There were usually between three to six tappings for each retort cycle, removing two to 12 kg per tap for a total production of around 40 kg per retort cycle. The final tap was just before the discharge and cleaning cycle.

The composition of the collected zinc changed over the batch cycle, being initially high in cadmium (0.1 per cent) and reporting high lead and iron contents towards the end of the cycle. Recovered metal was generally cooled and liquated to separate lead and iron, giving a product of 1.1 to 1.2 per cent lead and less than 0.025 per cent iron.

The firing of the furnace and control of temperature was an art to achieve a reasonably uniform distillation rate over the cycle and to minimise retort failure. Furnace temperature was progressively

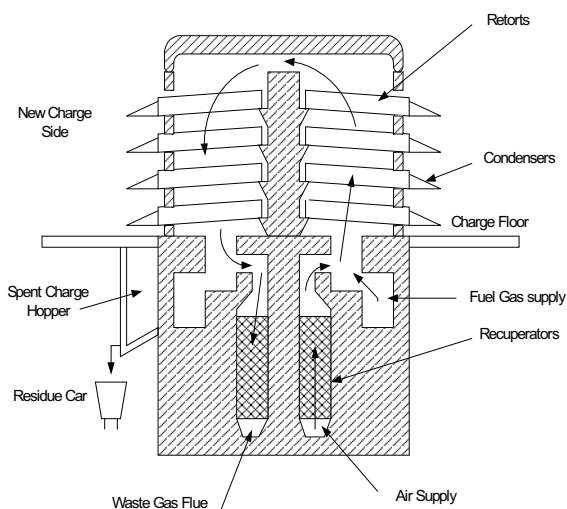


FIG 13.2 - Horizontal retort plant layout.

raised from around 1000°C after charging to around 1350°C at the end of the cycle. Retort temperatures were approximately 100°C lower. Usually one side of the furnace would be near the end of the cycle and gases from that side would pass to the opposite side at the early stages of the cycle. Exhaust gases generally discharged through a checker brick recuperator. Retort residues contained between five and 20 per cent zinc, but typically around 13 per cent, and average zinc deportment is shown in Table 13.1.

TABLE 13.1
Zinc deportment in a horizontal retort.

Component	48 hr cycle	24 hr cycle
Loss in retort residues	6%	10%
Blue Powder	5%	5%
Casting drosses	5%	5%
Seal clay, condensers and retorts	7%	5%
Gas leaks - fume	2%	3%
Product metal	75%	72%

Blue powder formed as un-agglomerated metal droplets in the condenser and was minimised by the use of salt in the charge. Blue powder, fume and drosses were recycled so that overall recovery of zinc from new feed to product metal on the above basis was of the order of 87 per cent for a 48 hour cycle, and 85 per cent for the 24 hour cycle.

In the later years of the retort process, various procedures were introduced to recover zinc from retort residues, such as magnetic separation, wet concentration and Waelz kiln processing. Reject and broken condensers also contained up to two per cent of input zinc and these were crushed and concentrated to yield a recycle material added to the retort mix. Alternatively, the crushed condensers could be processed in a Waelz kiln. Many old retort plant sites have an environmental legacy of large dumps of old retort residues with resulting leaching of zinc and cadmium into groundwaters.

The horizontal retort process was labour intensive with a heavy manual load for batch charging, metal tapping and retort cleaning operations. A crew was generally around 14 per furnace side of 400 retorts. This represents 16 tonne of zinc metal per cycle and corresponds with 336 person hours or 21 person hours per tonne. There was additional labour for charge preparation, retort manufacture and services, further increasing the total labour for the horizontal retort process. This compares with five person hours per tonne for the electrolytic process and clearly illustrates one key reason why the technology became obsolete. Overall energy use is indicated in Table 13.2.

TABLE 13.2
Energy use for the Horizontal Retort Process.

Component	Amount per t of zinc	Energy Consumption MJ per tonne of zinc
Reduction carbon	450 kg	14 000
Heating coal	1800 kg	59 000
Electric power	140 kWh	500
Total		73 500

The total energy use was more than double the equivalent thermal energy requirements for the electrolytic process based on 35 per cent conversion efficiency of thermal energy to electrical energy (3800 kWh/t or 13 700 MJ/t electrical energy, which is equivalent to 39 150 MJ/t thermal energy). This was another compelling reason for obsolescence of the horizontal retort process.

THE VERTICAL RETORT PROCESS

The vertical retort was developed in the 1920s as a continuous retorting process by the New Jersey Zinc Company. The problems facing its development were the high heat flux required through the walls of the retort, and the continuous condensation of zinc from retort gases at relatively high rates in comparison with the horizontal retort process. Designs of the retort primarily followed the principles of coking ovens, using a vertical narrow chamber with combustion chambers on either side and heat transmitted through the parallel side walls. However, the heat flux required is much higher for zinc reduction and vaporisation than for coke production, so a highly conductive refractory wall must be used. Both high strength and high thermal conductivity at elevated temperatures led to the use of silicon carbide. The walls are constructed of tongue and grooved bricks, which are free to move in slots contained in the side walls of the furnace. Operating temperatures are 1300 to 1350°C in the combustion chambers, giving temperatures of 1200 to 1250°C within the retorts.

Heat transfer from the walls of the retort to the charge is largely by radiation. Because of this, the charge is formed into briquettes and since each briquette should be able to 'see' the wall, the retort chamber must be narrow, and the briquettes must be sized appropriately and have sufficient strength to avoid break-down in moving through the chamber.

The typical vertical shaft is ten to 12 m high with a rectangular cross section of 1.5 to 2.2 m long and 300 mm wide. Walls are around 115 mm thick. Each furnace block contains about eight retorts with a zinc production capacity of around seven tonne per day per retort. A schematic arrangement of the standard retort is given in Figure 13.3.

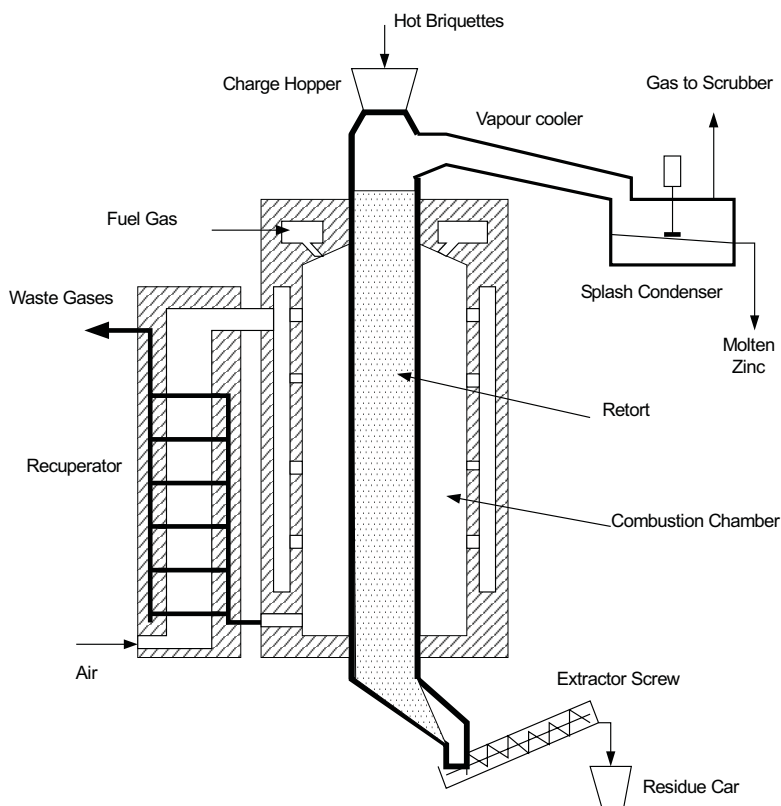


FIG 13.3 - Vertical retort process.

Charge Preparation

The need for strong, consistently sized briquettes made up of oxidised zinc materials and carbon requires considerable preparation; involving the sintering of concentrates, the formation of briquettes from sinter, bituminous coal and binders, and the coking of the briquettes at temperatures of around 800°C.

Feed to briquetting consists of sinter, roaster calcines, bituminous coal, clay and binder. The binders commonly used were sulfite tars from paper pulp manufacture. The combined ingredients are ground and mixed to provide a plastic mass ready for forming into briquettes using a roll press.

Optimum briquettes are pillow shaped, approximately 100 mm long, 75 mm wide and 65 mm thick, weighing about 0.5 kg.

The green briquettes are fed to a coking furnace in which the temperature is raised to around 800°C by controlled autogenous combustion of the volatile components of the coal. The coking furnace was commonly a multi-stepped grate design. In some plant designs the coking furnace was heated by combustion of retort gases, but autogenous operation was generally preferred to reduce the dependence of the coking operation on the operation of the retorts. Hot briquettes are transferred directly from the coking furnace to the retorts at a temperature of around 700°C. It was also the practice to charge metallic zinc scrap directly to the retorts and this can represent up to 20 per cent of the total feed.

Retort Operation

The briquette charge is added periodically through mechanical seals in the top of the retorts from an overhead charge car. Since residues are withdrawn continuously, the level of charge in the top section of the retort varies and the top 2 m of the retort projects above the combustion chamber and is not heated. Residues are withdrawn using a screw extractor which is commonly water sealed. However a small controlled air purge is admitted at the base of the retort to prevent downward diffusion of zinc vapours. Because of the high residual carbon content, oxygen contained in purge air is rapidly converted to CO.

The combustion chambers are fired with natural gas or producer gas supplemented with retort gas, which can supply up to 30 per cent of the heat requirements. In order to ensure maximum retort life it is most important to maintain uniform temperatures throughout the combustion chamber. To achieve this air is added at up to six levels in the chamber and can control temperatures between 1300 and 1320°C. Combustion gases pass through recuperators to heat incoming air and are discharged at around 500 to 600°C. After cooling in a humidifying tower, gases pass through a bag filter and can be discharged.

Gases from the retort are drawn through the condenser chamber in which a bath of molten zinc is sprayed into the gas stream and onto the chamber walls using a rotating graphite impeller. Zinc from the hot retort gases condenses onto the colder zinc spray and molten zinc running down the condenser walls, and is incorporated into the condenser bath. The bath constantly overflows to a collection launder and into a common holding furnace. The condenser bath is maintained at a temperature of around 550°C using water-cooled coils variably immersed into the bath. The immersion depth is varied to control bath temperature. About 95 per cent of the zinc vapour is condensed as liquid metal, three to four per cent reports as 'blue powder' accumulating in the condenser and one to two per cent remains in the residual gas stream.

Gas is drawn from the retort through the system using a venturi ejector, which also serves to scrub the gas and remove residual zinc. The cleaned gas is then directed into the fuel gas supply to the combustion chambers. The condenser needs to be regularly cleaned to remove oxide accretions and accumulated blue powder. Together with recovered residues, these materials are recycled to charge preparation.

In the upper sections of the retort there is a tendency for zinc oxide to form hard accretions on the walls of the charge section and on the roof. The presence of aluminium in metallic scrap feed can also

cause hard alumina accretions, which reduce heat transfer and are difficult to remove. Cleaning frequency varies depending on feeds and the use of scrap but can be between two and six weeks. Both the retort and condenser are cleaned at the same time.

Retort Residues and Further Processing

Retort residues contain typically five per cent Zn plus other base and precious metal values and between 30 and 50 per cent carbon. High levels of residual carbon are necessary to prevent the melting of the briquettes on passage through the retort.

It was common practice to further process the residues in a small blast furnace, utilising the contained carbon and producing a slag for disposal and a matte containing copper and precious metals. Zinc and lead are generally volatilised and collected as fume from the blast furnace gases. The fume is recycled to the retort charge preparation. If not processed in this way, retort residues presented a significant disposal problem due to the tendency for spontaneous combustion in dumps and due to leaching problems and the contamination of ground waters.

Vertical Retort Performance

The vertical retort is considerably more efficient than the horizontal retort, consuming about half the carbon and with a labour requirement of about 7.5 person hours per tonne of zinc produced, compared with 21 person hours per tonne for the horizontal retort.

Equipment requirements and related maintenance costs are relatively high and containment of dust and fumes is difficult, particularly in the handling of hot briquettes and retort residues. The briquette feed is also limited to a maximum of ten per cent iron content, since above this level there is a tendency to form plates of iron in the retorts, which obstructs the movement of briquettes. As with the horizontal retort, only Prime Western Grade zinc is produced with a typical lead content of 0.1 to 0.2 per cent, requiring further refining to produce premium grades. The vertical retort is no longer competitive and most of the world's plants have been closed, leaving only one or two still reportedly operating in China.

THE ELECTROTHERMIC RETORT PROCESS

The electrothermic retort generates heat for the retorting process internally by passage of an electric current through the charge, thus avoiding the need for heat transfer through the walls of the retort. It was developed by the St Joseph's Lead Company in the 1920s, as an alternative to the Horizontal Retort Process.

There were many early attempts at electrothermic retorting from the 1880s and most involved an electric arc furnace, with pioneering work by deLaval at Trollhattan in Sweden in 1898. Many subsequent attempts were made and most failed, due to the difficulty of condensing relatively large volumes of zinc vapour, particularly from dusty gases generated from an open arc.

Electrical resistance heating would overcome the complications of dust generation and formed the basis of a practical process. Power is supplied through a series of graphite electrodes located at the top and at the base of a shaft furnace with a spacing of about eight to 10 m. The larger standard furnace design is 2.4 m diameter with eight electrodes at the top and eight at the bottom. This furnace has a capacity of 72 tonnes of zinc per day. An arrangement of the electrothermic retort is shown in Figure 13.4.

The furnace is normally charged with high-grade sinter sized between five and 20 mm, and coke at about equal volume to the sinter. Coke use is approximately 0.8 tonne per tonne of zinc recovered.

It is common to also charge briquettes and scrap metallic zinc to supplement sinter. However, most materials such as EAF dusts and calcines are all passed through the sinter plant, since the production and use of a high quality sinter is most important.

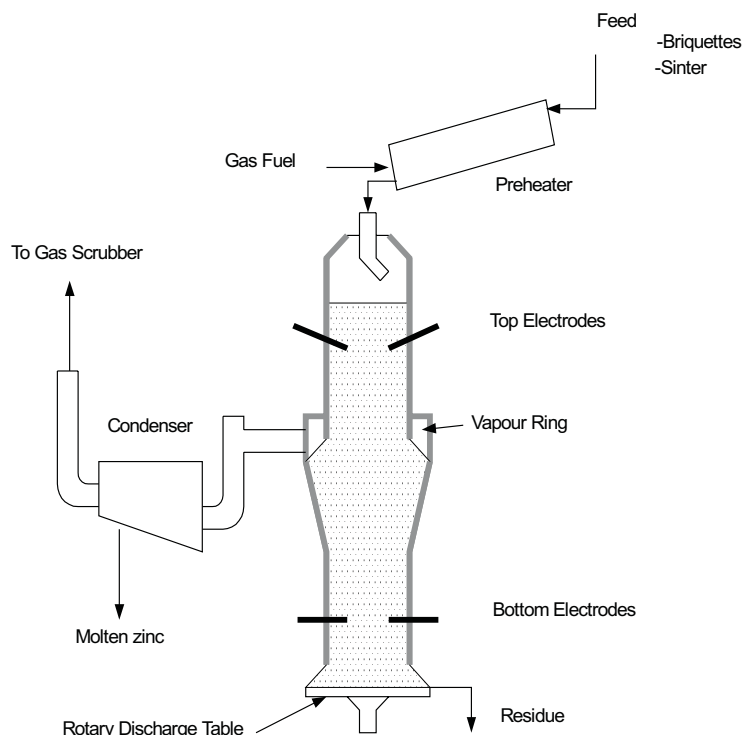


FIG 13.4 - Electrothermic retort process.

Feed is preheated to around 750°C in a rotary kiln fired with retort gas, and is dropped continuously into the furnace through a rotary distribution valve. This device allows the coarse fraction of the feed to accumulate in the centre of the furnace and the finer fraction to accumulate near the walls. This arrangement established a temperature distribution that is highest in the centre (1300 to 1400°C) and lowest at the walls (900 to 950°C). The base of the shaft consists of a rotary discharge table that can be varied in speed to control the rate of throughput of the charge.

Furnace power input is up to 10 MW for the larger unit with eight electrode pairs, at a supply voltage of 240 volts. This represents an electrical energy consumption of close to 3000 kWh/t of zinc produced.

The vapours generated in the shaft are approximately 50 per cent zinc by volume. These gases are collected in an annular ring located about one third of the electrode separation distance down from the top electrodes, and are drawn off into the zinc condenser. Gas temperature entering the condenser is around 900°C. The condenser developed for the electrothermic retort was based on the steam jet condenser principle in which vapour is drawn through a jet into a pool of molten zinc (see Figure 11.10). The zinc bath is cooled by immersing water cooled U tubes into the zinc bath under temperature control to between 480 and 500°C. Condenser efficiency is about 93 per cent. The furnace annular and condenser are manufactured from silicon carbide bricks.

Gas from the condenser is scrubbed to recover any residual zinc and is passed through a vacuum pump and delivered as fuel gas to the furnace charge preheating kiln. Composition of retort gas is 80 per cent CO, three per cent CO₂ and 17 per cent N₂.

The service life of a furnace can be quite low at four to five months with 30 days required for the rebuild. This corresponds with an availability of 75 per cent. The corresponding annual production for the larger furnace at 72 tonne of zinc per day would be close to 20 000 tonne per year.

The residues discharged from the furnace contain up to 15 per cent zinc and require reprocessing for recovery and recycle of zinc in order to achieve acceptable overall zinc recovery. Residue processing consists of initial crushing and screening with the coarse fraction rejected as slag. The intermediate fraction at around 8 mm sizing is predominantly coke and is recycled to the furnace. The fines are magnetically separated to remove metallic iron leaving a fine fraction rich in zinc and coke fines that is returned to the sinter plant. Heavy media and pneumatic separation have also been used to improve the recovery of zinc and carbon and the rejection of waste.

As with other retorting processes, there are limits to the iron content of feeds due to complications caused by the formation of metallic iron. Even so, it is necessary to maintain an optimum iron balance through the furnace, which is controlled by adjustment of the magnetic separators to permit more or less iron to be recycled.

Performance parameters for the electrothermic retort are typically as follows:

Total electric power per tonne of zinc produced =	3200 kWh
(furnace only) =	2500 kWh
Coke use per tonne of zinc produced =	0.6 tonne
Graphite electrodes per tonne of zinc produced =	1.1 kg
Man hours per tonne of zinc produced =	18

The electrothermic retort is a high cost process with poor equipment availability and relies on the use of low cost electric power. Few plants using this process were built and only one remains in operation at the Monaca smelter in the USA.

Fuming in the Electrothermic Retort

A variant of the electrothermic retort process is used by the Toho Zinc Company at Onahama, Japan, to treat electric arc furnace-steel plant dusts, but producing zinc oxide instead of condensing to zinc metal. Gas drawn from the retort is mixed with air to oxidise the zinc vapour to zinc oxide fume, which is collected in bag filters after gas cooling.

REFERENCES

Suggested Reading

Mathewson, C H, 1959. ZINC – The Science and Technology of the Metal, Its Alloys and Compounds, pp 225-264 (Rheinhold:New York).

Blast Furnace Production of Zinc

DEVELOPMENT OF THE ZINC BLAST FURNACE

As indicated in Chapter 11, it is not practical to form molten zinc metal directly in any carbothermic reduction process; it is only possible to produce zinc as vapour. This applies to the blast furnace, as well as retorting processes, and the blast furnace differs from retorting processes only by the fact that heat is generated internally by combustion of carbon using oxygen from an air blast. As a result, furnace gases are of high volume with low concentrations of zinc vapour at less than ten per cent, compared with around 40 to 50 per cent for retorting processes, and with much greater relative levels of CO and CO₂. This greatly increases the difficulty of condensing zinc from the furnace gases and avoiding re-oxidation.

There were many unsuccessful attempts at blast furnace production of zinc, but it was not until publication of a thermodynamic analysis of the problem by Maier in 1930 detailing the principles outlined in Chapter 11, that the requirements of a practical process were realised (Maier, 1930).

The essence of the blast furnace production of zinc is the maintenance of high enough temperatures in the upper sections of the furnace to prevent re-oxidation of zinc vapour and the need to effect condensation by rapidly chilling the gas and condensing zinc before it has time to re-oxidise. This is possible with the kinetics of oxidation of zinc vapour by CO₂, but is difficult in the presence of water vapour since oxidation rates are much higher. The development of the lead splash condenser by the Imperial Smelting Corporation at Avonmouth (UK) in 1943 paved the way for successful development of this technology. The use of molten lead as the cooling medium also provides a solvent for zinc and provides an absorption or scrubbing action rather than direct condensation to liquid zinc.

It also became clear during initial development of the process that simultaneous production of lead metal from the base of the furnace was possible as lead volatilisation can be minimised by control of the sulfur content of sinter feed to the furnace (PbS is the most volatile lead compound).

The initial furnace developments progressed from a standard water-jacketed lead blast furnace of rectangular cross section, but with a closed and sealed top. A number of pilot plants were constructed at Avonmouth in the 1940s and 1950s followed by the first commercial plant at Swansea in 1960. A number of units based on this design were soon licensed at various sites around the world and a larger design was completed and installed at Avonmouth in 1967. Subsequently, furnaces have evolved by modification to the lower shaft and by progressive enlargement, taking advantage of the periodic need to rebrick and rebuild the furnaces every five or so years. There have thus been significant departures from the original standard design and an expansion in its capabilities. A list of the 13 furnaces in operation as at 2000 is given in Table 14.1 (Lee, 2000).

Following a prolonged period of low metal prices and low smelter treatment charges in the early 2000s, the economics of a number of these plants deteriorated to the point where it was no longer possible to continue operation and the plants were closed (Avonmouth, Cockle Creek, and Noyelles Godault).

PROCESS DESCRIPTION

A general process flow sheet is shown in Figure 14.1. Furnace feed is prepared from sulfide concentrates as sinter using a standard updraught sintering machine with attached sulfuric acid plant. High quality sinter in terms of uniform coarse sizing and strength is essential for good performance and efficient operation of the blast furnace. Details of sintering operations are given in Chapter 12.

TABLE 14.1
ISP smelters in operation in 2000 (Lee, 2000).

Location	Country	Shaft A ream 2	Year Started	Max Zinc Output t/y	Max Lead Output t/y
Avonmouth	UK	27.2	1967	105 700	51 200
Chanderiya	India	21.5	1991	61 400	31 000
Cockle Creek	Australia	24.2	1961	97 300	40 700
Copsa Mica	Romania	17.2	1966	34 100	17 100
Duisburg	Germany	19.3	1966	97 400	45 100
Hachinohe	Japan	27.3	1969	114 400	52 100
Harima	Japan	19.4	1966	88 900	28 600
Miasteczko	Poland	19.0	1972	84 600	36 000
Noyelles Godault	France	24.6	1962	115 700	48 300
Porto Vesme	Italy	19.0	1972	84 600	36 000
Shaoguan No1	China	18.7	1975	81 500	34 800
Shaoguan No2	China	17.2	1996	70 900	31 900
Veles	Macedonia	17.2	1973	59 700	30 500

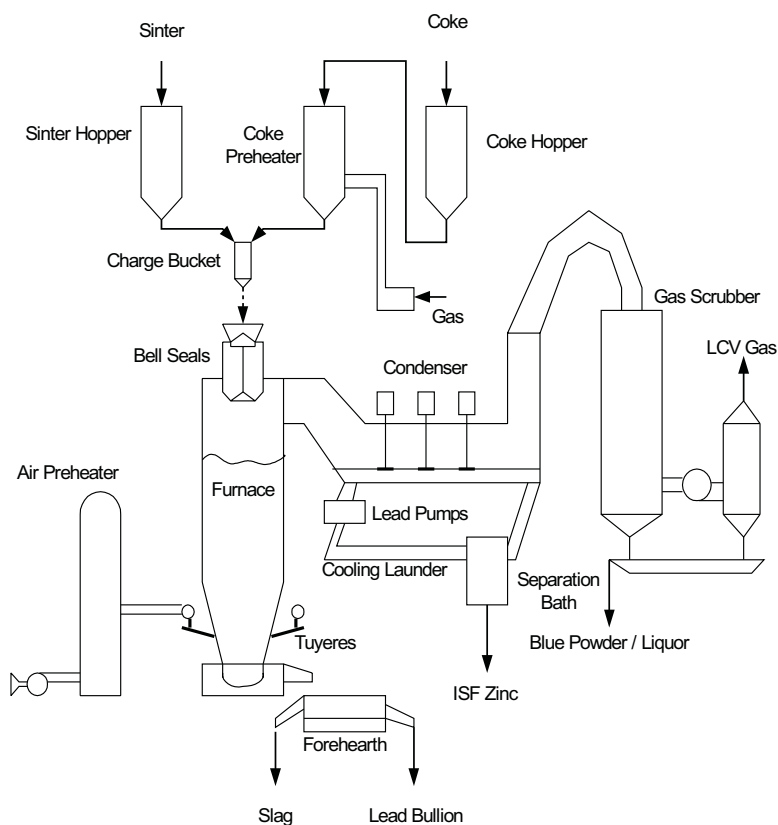


FIG 14.1 - Schematic layout of the imperial smelting process.

The standard furnace is a rectangular shaft constructed of a steel casing cooled externally by water shower and lined with refractory brick. Original dimensions were 6.3 m × 3.2 m at the outer steel casing and 17.1 m² upper shaft cross section within the brick lining. The furnace width narrows progressively to the hearth. Above the hearth are two opposing rows of tuyeres (one row on each side of the furnace), inclined towards the hearth and with around eight tuyeres in each side. Tuyere nozzles are made of copper with annular water-cooling channels. Air injected through the tuyeres is generally preheated to between 800 and 1000°C using Cowper stove recuperators and heated by combustion of the CO from furnace off-gases. Preheat is an important means of increasing furnace capacity and it has been reported that 100°C of preheat is equivalent to a three to five per cent increase in furnace capacity (Lee, 2000).

The top of the furnace is sealed and gases are taken through a side off-take to the condenser chamber. The standard furnace has one condenser chamber whereas the larger Avonmouth furnace design incorporated two condenser chambers located at opposite sides of the furnace.

Furnace feed consists primarily of sinter of the appropriate composition to give the required slag formulation, and coke preheated to around 700°C. Direct feeds such as briquettes made from zinc oxides, and metallic scrap can also be added to the furnace feed. Feed is charged to the furnace using weighed buckets, which are dumped into a double ‘bell seal’ hopper arrangement located in the furnace roof. The bell seals are water cooled steel construction and efficient sealing is very important.

At the tuyere zone of the furnace, carbon combustion takes place forming CO and generating most of the heat required to operate the furnace. Temperatures up to 1600°C are generated in the blast zone or tuyere raceways. As gases rise through the shaft, zinc oxides are reduced by CO and carbon is consumed by the CO₂ so generated to reform CO. These reactions are endothermic and temperatures decline towards the top of the shaft.

Zinc is reduced from the sinter as it moves down the shaft and is aided by an open porous sinter structure. When the sinter melts it trickles into the slag pool contained in the furnace hearth from where further zinc reduction takes place but at a lower rate. As a consequence, a higher sinter melting temperature can assist zinc reduction capacity, however the increase in throughput and temperature (or intensity of operation) can lead to greater difficulty in control. Most ISFs operate with a slag melting temperature of around 1200°C. Increasing the lime content of the slag can be used to raise the melting point of the slag and increase the activity of dissolved ZnO. Sinter composition ratios are commonly targeted at:

FeO: SiO ₂	2.7:1
CaO: SiO ₂	1.4:1
FeO: (CaO+SiO ₂ +Al ₂ O ₃)	1.1: 1

Coke will usually add significant quantities of silica (up to 50 per cent of sinter feed amounts) and will alter these ratios for blast furnace slag, which is the ultimate target. Slag and bullion are tapped from the furnace hearth into a forehearth where they are separated. Slag flows from the forehearth into a granulation launder and lead bullion flows to a lead ‘kettle’ of around 100 tonne capacity either directly or via batch ladles. The bullion is allowed to cool in the kettle to separate a copper-lead dross, reducing the copper content to around 0.2 per cent. The resulting lead bullion is then cast into blocks of up to four tonne each for transfer or sale to a lead refinery. Lead reduction tends to occur in the top zone of the furnace by reaction of lead oxides with zinc vapour and with CO. The reactions are endothermic.

To ensure that the temperature of the gas stream leaving the top of the furnace does not fall below a critical level where re-oxidation of zinc occurs, some air is introduced to burn CO and generate additional heat (‘top air’). Generally the critical temperature to prevent re-oxidation is around 950°C. Although the action of air injection does generate higher CO₂ concentrations and increases the potential for zinc re-oxidation, this is offset by the effect of the temperature increase achieved. Top air can represent around 12 per cent of the air volume injected through the tuyeres.

Gas leaving the furnace generally has the composition of five to seven per cent Zn, 16 to 18 per cent CO, ten to 13 per cent CO₂ and should have a temperature of close to 1000°C.

The lead splash condenser consists of a chamber approximately 8.5 m long $\times$ 5.5 m wide $\times$ 1.15 m high, and contains a pool of lead 0.4 m deep. Vertical baffles divide the chamber into four sections. Each section is fitted with two rotors located at the surface of the lead pool and driven by a vertical shaft projecting up through the roof to the electric motor drives. The inclined blades of the rotor throw up a spray of lead droplets into the gas stream, scrubbing out zinc and cooling the gas from around 1000°C at the inlet to around 500°C at the outlet. Molten lead is continuously circulated through the condenser, exiting at a temperature of 550°C and containing approximately 2.5 per cent zinc. The hot lead flows through a cooling launder where the temperature is reduced to 450°C at which point the solubility of zinc is reduced to 2.1 per cent (see Table 11.3). The lead flows to a settling bath where excess zinc floats to the surface and is separated using an overflow/underflow weir arrangement. Separated liquid zinc at 98.6 per cent zinc content is pumped to a holding furnace prior to refining and the cooled lead is circulated back to the condenser. The cooling launders may consist of a water jacketed launder, but improved and later designs use immersed water cooling tubes, which may be raised or lowered into the molten lead stream to achieve precise temperature control.

Dust carried over in the gas stream from the furnace forms a dross on the surface of the lead pool. Dross flows out of the condenser on the lead stream and is collected by skimming from the surface of the hot lead sump. It is important to keep the lead surface in the condenser as free as possible from dross accumulation since it interferes with the action of the rotors and the efficient spraying of lead into the gas stream. Poor quality sinter will lead to excessive dust carry-over in the gas stream and increased levels of dross formation.

A small portion of the zinc entering the condenser is oxidised by the CO₂ to form a zinc oxide fume. The fume can serve as nuclei for the condensation of zinc to form a fine fog of zinc droplets, which are not collected by the lead and are carried out of the condenser in the gas stream. Additionally, some uncondensed zinc vapour will remain in the gas stream. The amount of zinc in these forms is critically dependent on the efficiency of the scrubbing process and the performance of the rotors. Factors that affect the rotor performance are their mechanical condition, the presence of dross and the control of lead level in the condenser in relation to the position of the rotor. The gas flow rate through the condenser will also affect condenser efficiency as capacity limits are approached.

The presence of volatile halide compounds and alkali metals in the gas stream from the furnace can give rise to hard accretions at the condenser entrance and on the impellers, as well as forming a sticky dross. Consequently there are limits in the level of halides contained in ISF feed materials. Gases exiting the condenser pass through a scrubbing system where solids containing zinc escaping the condenser are collected as 'blue powder'.

Both condenser dross and blue powder contain approximately 30 per cent zinc and can each represent around four per cent of zinc throughput, giving 92 per cent recovery of zinc to the condenser as molten zinc metal (termed ISF zinc). Both these streams are recycled to the sinter plant and represent a loss in first pass recovery of zinc rather than a loss of overall recovery. As well as first pass recovery loss, the presence of dross can also interfere with condenser operation, leading to reduced efficiency and increased formation of blue powder.

Lead is lost from the condenser system in the product zinc stream, as dross, and as carryover condenser spray captured with blue powder, and must be made up by the addition of refined lead to the circulating lead stream. Apart from the lead contained in Prime Western Grade zinc, the lead lost from the condenser eventually reports to, and is recovered in ISF bullion.

SLAG COMPOSITION

There are limits to the level of zinc in final slag since as the oxygen potential is lowered to reduce more zinc, the tendency to reduce FeO and form iron is increased. At slag temperatures of 1350°C the presence of metallic iron can cause considerable difficulties in the tapping process. Generally zinc levels are not reduced much below six per cent in final slag for this reason.

Apart from the zinc content, slag composition is important for control of the appropriate melting point and viscosity of the slag, to ensure suitable operation of the hearth, and the ability to tap the furnace and achieve good separation of slag and bullion. Composition adjustment is made by the addition of fluxing components to the sinter feed, but can also dictate the concentrate feed mix and place limits on the intake of particular feed materials. Ratios of major components are targeted in sinter as indicated under Process Description in this chapter, but additional amounts of some components such as silica will be sourced from the coke and shift these ratios for slag. Slag compositions will vary depending on available feeds to the smelter but are typically as shown in Table 14.2 with a melting point of around 1220°C.

TABLE 14.2
Typical ISF Slag Composition.

CaO	18.5 %
SiO ₂	19.5 %
FeO	41.5 %
ZnO	9.5 %
PbO	1 %
Al ₂ O ₃	8 %
MgO	0.5 %
Other	1.5 %

Component ratio	Typical value	Range in values
CaO : SiO ₂	0.95	0.8 - 1.4
FeO : SiO ₂	2.1	1.8 - 2.9
FeO : (CaO+SiO ₂ +Al ₂ O ₃)	0.9	0.7 - 1.2

The chemistry of slags, the various phases that can be present and their interactions, is complex and minor variations of some components can have significant effects. For instance Al₂O₃ at high levels results in the precipitation of Hercynite (FeO.Al₂O₃), which raises the melting point of the slag but lowers the potential to form metallic iron. At low concentrations of Al₂O₃ there is increased potential to form metallic iron with associated problems. Such subtle effects can have a significant impact on the hearth and tapping operations

IMPURITIES AND ZINC METAL QUALITY

The ISF has the inherent advantage that zinc is separated from other components of the feed by vapourisation and hence only volatile elements and compounds can be collected with the product zinc. Although some metals may not be volatile, their compounds, such as halides, can be and this can lead to product zinc contamination. The principle contamination is by lead due to its use as a collector in the lead splash condenser. The product zinc is thus saturated with lead.

Cadmium metal is more volatile than zinc, consequently all of the cadmium contained in furnace feed reports to the product zinc. A significant proportion of the cadmium in raw materials will fume during sintering and can be separated at that stage, thus reducing the final level in furnace zinc and reducing the load on the refining stage.

Tin compounds are volatile and 20 per cent of furnace input can report to product zinc, with the balance split between slag and bullion. Tin will be separated by distillation refining of the zinc, but any Prime Western Grade metal produced (un-distilled component) will retain the tin content of furnace zinc and can exceed specification limits of 0.02 per cent. Restriction of feed materials may be required to maintain levels within specification.

Some volatile elements, such as arsenic and antimony, can be captured from the rising furnace gases by molten lead forming at the top of the furnace shaft and trickling down to the hearth. The presence of lead therefore reduces the levels of these metals in furnace zinc. Arsenic then tends to combine with iron in the furnace hearth to form a speiss, which leaves the furnace with slag.

Other elements such as copper, silver, gold and bismuth are efficiently collected by lead bullion. About 80 per cent of the copper in furnace feed is captured and is later separated as a copper dross leaving around ten per cent in the de-coppered bullion.

EVOLUTION OF FURNACE DESIGN AND OPERATION

As indicated above, there has been progressive evolutionary improvement in the design and capability of the standard blast furnace and considerable expansion in its capacity. The original standard furnace had an upper shaft cross-section of 17.1 m^2 constructed of a refractory lined steel shell ($6.3 \text{ m} \times 3.2 \text{ m}$), which was cooled externally by means of a water shower. The lower shaft narrowed at the tuyere level and was constructed of two rows of water jackets. 26 tuyeres as two opposing rows each of 13 were used at relatively low intensity or blast rate, in keeping with standard lead blast furnace designs. Figure 14.2 illustrates the general vertical cross section of the original furnaces.

The formation of accretions in the shaft was a particularly serious problem with the early design, aggravated by water leaks from the jackets forming the lower shaft. This problem became more significant as attempts were made to increase the blast intensity and productivity of the furnace. It was recognised that the required characteristics of the furnace were more akin to the higher intensity iron blast furnace than to the lead blast furnace. These characteristics are:

- the higher carbon requirements per unit of metal produced,
- the highly reducing conditions required,
- the use of blast air preheat for fuel efficiency, and
- the higher blast rates required for furnace productivity.

It was recognised that the narrow hearth configuration as shown in Figure 14.2 was unsuitable for high intensity operation and for maximum retention of slag in the hearth in order to minimise the final zinc content of slag. This latter requirement followed from the recognition that a significant level of ZnO reduction occurred from the slag pool held in the hearth. As a consequence of these issues the hearth of the furnace was widened, water jackets in the lower shaft were replaced with a shower cooled steel casing, the number of tuyeres was increased and the blast rate was increased. Raceways developed at the tuyere level as in the iron blast furnace, creating greater mobility of coke at the tuyere zone and greatly increasing the interaction with the slag pool. The general cross section of the furnace changed to that shown in Figure 14.3.

The formation of a zone of solid fused material in the centre of the furnace just above the tuyere zone (or 'deadman') provides support for the charge column above but, if excessive, restricts the flow of material and gases, thus limiting the capacity of the furnace. The extent of this formation is controlled

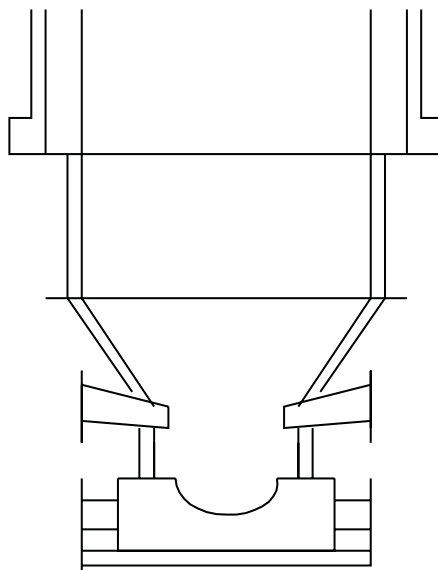


FIG 14.2 - Original ISP furnace configuration water jackets in lower shaft.

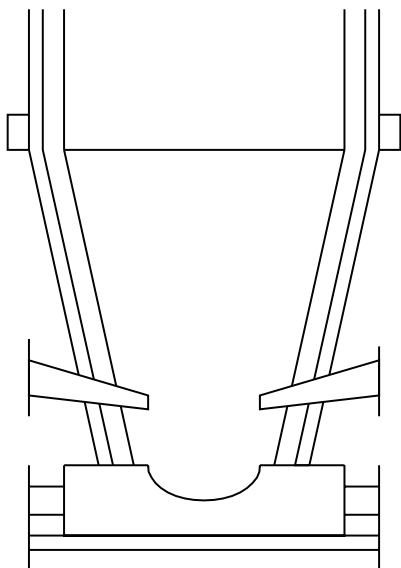


FIG 14.3 - Later configuration of the lower shaft.

by limiting the separation between opposing tuyeres, as dictated by the blast velocity and hence blast volume and the number of tuyeres installed. The lower sections of the 'deadman' may be composed of relatively high melting point iron and speiss, as well as unreacted coke.

As the blast rate is increased, the raceway size increases and greater separation is required to prevent excessive overlap of adjacent raceways. Hence, for a given furnace, the number of tuyeres must be reduced. To limit excessive overlap of opposing tuyere raceways, it is necessary to reduce velocity by increasing the diameter of the tuyeres. However, it is necessary to ensure that there is a minimum degree of overlap under all operating conditions. There are thus a number of complex interactions in furnace design and a balance between the blast rate, tuyere diameter, the number of tuyeres, and the furnace width, which determine capacity and the efficiency of zinc recovery

from the feed material. Assessment of raceway coverage is an important tool in design and can be done using an equation developed by Włodarczyk as published by Harris (1981).

The standard furnace now has typically 16 tuyeres as two rows of eight per side. The angle of the tuyeres to the horizontal is also a parameter of some importance, although it varies between individual plants. High angles will give greater interaction with the slag pool, but will induce high wear rates on the furnace hearth refractories. Initial furnace designs had a tuyere angle of 10° but this has increased to between 15 and 20°.

Accretions

A particular problem with the ISF is the tendency to form accretions of zinc oxide by reoxidation of zinc vapour in colder areas of the furnace, which essentially means the furnace walls. Critical areas are around the upper surface of the charge, the furnace roof and condenser entry. Accretions grow and progressively reduce the cross-sectional area and capacity of the furnace. Extensive growth can also generate significant hoop stresses on the furnace and can result in splitting of the casing and lifting of upper sections of the shaft. Movements in the upper shaft can affect the attachment to the condenser and if movement is transferred to the condenser can severely impact on its performance by affecting lead levels. Regular shutdown time for the cleaning of accretions is consequently necessary, and is usually on a three to six week cycle. Explosives may be used to remove accretions from the furnace shaft, but in other areas manual cleaning using jackhammers is necessary. As an alternative to blasting, the furnace may be burnt down to tuyere level with a high coke charge and the offtake temperature is allowed to rise so as to remove accretions. This action tends to marginally reduce the life of shaft refractories and may risk damage to the furnace casing.

Slag and Bullion Tapping

The original ISF design was based on batch tapping with a variable level of slag and bullion in the base of the furnace, and most operating furnaces remain with this configuration. However as indicated above, the interaction of the slag pool with the tuyere raceways is important in maximising the

reduction and elimination of zinc from the slag. Hence it can be argued that control of the slag level has important implications and steady control can only be achieved with continuous tapping. Varying levels of slag caused by intermittent tapping will also cause varying back pressure on the blast air supply, thus varying the blast rate. There are also implications for the separation of lead from slag. When tapping is at a high rate and flow through the forehearth is high, losses of lead, copper and precious metals in slag will be higher. There are thus significant advantages in adopting continuous tapping. However, experience has shown that although the above advantages can be achieved, a different flow regime and phase distribution occurs within the furnace, and this can lead to difficulties with the discharge of speiss from the furnace with slag. Iron speiss can be solid within the hearth and form a layer between the lead and slag at the end of the hearth opposite the tapping position. To avoid this, it is necessary to achieve a high level of mixing and hence strong interaction of the tuyere raceways with the slag pool, in turn requiring increased inclination of the tuyeres (Holliday *et al*, 1987).

The higher pressure operation of the ISF, compared with the lead blast furnace, means that weir heights in the forehearth are greater and there is more difficulty in maintaining the tapping hole open.

COKE USE AND FURNACE CAPACITY

Coke represents the primary fuel for the process and is the major cost item. Its efficient use is of key importance. Coke needs to be sufficiently strong to avoid degradation during handling and passage through the preheaters and furnace shaft. Volatile content should be low to avoid the presence of hydrogen, and reactivity should be reasonably low. A highly reactive coke causes the reduction zone to move to higher levels in the furnace and reduces the amount of carbon reaching the tuyere zone, thus lowering the temperature at the base of the furnace. This lowers the reduction of zinc from the slag pool and raises the loss of zinc in slag. The lower temperatures can also create difficulties with slag viscosity and the tapping of slag from the furnace. These effects can be overcome by increasing the coke consumption, but it is preferable to use a low reactivity coke.

As indicated, coke is preheated to 700 or 800°C in a shaft in countercurrent flow to combustion products from the burning of condenser gas. Since the exit gas conditions for the furnace are relatively well defined in terms of temperature, CO and CO₂ contents, the carbon consumption of the furnace will be directly related to oxygen input in blast air and top air. The furnace can in fact be defined closely in terms of its coke burning capacity. This can be increased per unit of oxygen supplied by preheating of the blast air and coke, and by oxygen enrichment of blast air, but a typical figure given average conditions as indicated above, is 1.2 kg of carbon per 1000 Nm³/h of oxygen input in blast air.

The maximum blast air input volume for the standard furnace of 17.2 m² upper shaft cross-section is close to 34 000 Nm³/h. The typical furnace blast maximum intensity is close to 2000 Nm³/h per m² of shaft area. On this basis such a standard furnace has the capacity to burn:

$$34\,000 \times 24 \times 21 \text{ per cent} \times 1.2 \times 10^{-3} = 205 \text{ tonne per day of carbon.}$$

For coke with a fixed carbon content of 85 per cent, this represents close to 240 tonne per day of coke as the maximum burning rate. Practical rates will be below this figure due to plant intensity and availability issues.

The manner in which carbon is utilised for zinc production is affected by heat balance issues as well as chemical requirements for metal reduction. The heat balance is influenced by the amount of slag produced, the blast preheat and the preheat achieved in coke and sinter. Apart from the quantity of zinc oxide reduced, the chemical factors include the lead and iron contents of sinter and the moisture entering the furnace in blast air and in sinter or additives. Based on typical operating conditions as indicated above, and a lead production of close to 50 per cent of the zinc production, the empirical formula used to relate carbon consumption to zinc production is given by Equation 14.1.

$$\text{Carbon consumed} = 0.655 \times \text{zinc produced} + 0.152 \times \text{slag produced} \quad (14.1)$$

For a typical slag production of 0.9 tonne per tonne of zinc produced, Equation 14.1 indicates a carbon to zinc ratio of 0.8 or a zinc to carbon ratio of 1.25. Hence the maximum zinc production from a standard furnace would be $205 \times 1.25 = 256$ tonne per day. This represents the zinc that can be produced in furnace gases to the condenser and is reduced in practice by inefficiencies, loss of plant availability for cleaning and breakdown, and by reduced intensity of operations for various reasons. For 92 per cent recovery of vapourised zinc to product metal and 90 per cent plant utilisation this will equate to an annual capacity of 77 400 tonne.

Fuel can be injected through the tuyeres either in the form of coke fines, or as pulverised coal, fuel oil or gas. This basically replaces lump coke and is done as a cost saving measure, rather than affecting production capacity. However, there can be offsets with the use of hydrogen containing fuels such as oil, natural gas and coal, which give rise to problems during condensation due to the reaction of zinc and water vapour. As an adjunct to this, the presence of water in blast air due to natural humidity can be a significant problem, firstly in consuming carbon in the lower shaft and later in causing condensation problems due to the presence of water vapour. Dehumidification of blast air can be justified in some circumstances. The impacts of a number of these factors were reviewed and modeled by Kellogg (1990).

Oxygen enrichment of blast air gives a marginal reduction in carbon use per tonne of zinc produced but a significant increase in capacity of the furnace of the order of four per cent extra zinc production per one per cent oxygen enrichment in blast air.

SUPPLEMENTARY FURNACE FEEDS

It is common practice to supplement sinter feed with briquettes produced from oxidised zinc materials and most notably from Waelz oxide. Other zinc rich residues, calcines and fumes can also be briquetted. It is important to produce a strong briquette that does not disintegrate on handling and in passage down through the furnace shaft. For this reason briquettes produced by hot forming (Chapter 16) are preferred. Most operators tend to use only a minor portion of their feed as briquettes at around ten per cent of zinc input, although the Duisburg smelter has used up to 30 per cent. The limitation on these materials is set by their content of halides and alkali metals. These materials are volatile and tend to form accretions, particularly at the furnace offtake and condenser inlet, as well as contributing to the formation of dross. A decline in condenser efficiency is reported with the increasing use of briquettes, from around 93 per cent with none, to around 86 per cent with 30 per cent of the charge as briquettes.

Metallic scrap or material with a high metallic content such as galvanisers ashes can be directly added to the furnace charge. The zinc metal content will melt and vapourise at the top of the shaft and directly report to the condenser. It does represent an endothermic heat sink at the top of the furnace, but otherwise has little impact on the operation of the shaft.

It is also feasible to inject powdered zinc oxides through the tuyeres of the furnace. The material is mixed with pulverised coal to provide additional fuel and is injected with air through lances inserted into the tuyeres. Not all the tuyeres need be used. This operation can also be facilitated by the use of oxygen injection at a level of about two per cent enrichment of blast air. Practical injection rates of 2 t/h per tuyere were demonstrated at the Avonmouth Smelter (Temple, 1980), representing about seven per cent of total production. This mode of operation was also practised at the Duisburg smelter.

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Thermal Refining of Zinc

Zinc produced by carbothermic reduction processes and vapour condensation contains significant levels of impurities and requires refining to meet market specifications. Principal impurities are lead and cadmium, but there can also be significant levels of iron, copper, arsenic, antimony and sometimes tin. Non-volatile elements can be present due to dust carryover from the reduction process to the condenser.

LIQUATION REFINING

Crude refining can be achieved by virtue of the reduced solubility of lead and iron as the temperature of molten zinc is reduced. The solubilities of lead and iron in molten zinc are shown in Table 15.1.

By slowly cooling the molten zinc to between 430 and 440°C over a period of 16 to 24 hours the lead content can be reduced to less than 1.2 per cent and the iron content to around 0.025 per cent. Three layers are formed with the refined zinc at the top, an intermediate layer of solid zinc-iron alloy and a lower layer of molten lead containing two to three per cent zinc. The zinc iron alloy contains around six per cent iron. A reverberatory furnace is used for this duty.

TABLE 15.1

Solubility of lead and iron in molten zinc.

Temperature °C	Lead %	Iron %
420	0.9	0.018
450	1.4	0.03
500	2.3	0.10
550	4.0	0.30
600	5.9	0.70

REFINING BY CHEMICAL PRECIPITATION

The addition of sodium metal to molten zinc precipitates arsenic as an arsenide, which can be oxidised and separated as a surface dross. Zinc from the ISF process can contain 0.05 per cent arsenic, and this can be reduced to 0.003 per cent by the addition of around 0.7 kg of sodium per tonne of zinc. Lead is also separated by sodium treatment to levels of around 0.5 per cent.

High levels of iron may also be removed by the addition of metallic aluminium in the ratio of 2:1 to the quantity of iron to be removed. Zinc is heated to 600°C and the aluminium added under a flux layer and stirred into the zinc. After cooling to 500°C and settling, an iron rich dross can be separated from the surface of the zinc. The technique also is useful for the removal of arsenic. Care needs to be taken with the handling of any arsenic containing drosses, since exposure to water may generate toxic arsine gas.

REFINING BY DISTILLATION

The boiling points of the principle elements of concern are zinc 907°C, cadmium 767°C, lead 1620°C and iron 3000°C. Distillation of impure zinc at atmospheric pressure will vapourise zinc and cadmium, but will essentially leave lead and iron with the residual zinc.

Early distillation refining techniques were based on re-distillation in horizontal retorts. However this represented only one separation stage and it was difficult to control impurities both from that viewpoint and from the effect of carry-over from the boiling retort. Inconsistent separation of lead, iron and other non-volatiles was achieved, but highly volatile cadmium was not separated. To obtain pure zinc, two separate distillations are required, the first to distil zinc and cadmium away from the low volatility elements of lead and iron, and the second to distil the more volatile cadmium away from zinc.

At its boiling point at atmospheric pressure (907°C), zinc naturally has a vapour pressure of 760 mm of Hg. At that temperature, lead has a vapour pressure of 0.3 mm of Hg, hence a small quantity of lead can transfer to zinc condensed from the vapour. Multi-stage counter-current distillation is therefore required in order to achieve high purity zinc metal.

In its quest for high purity zinc for the preparation of alloys, the New Jersey Zinc Company developed the reflux distillation column in 1930. The distillation columns were constructed from silicon carbide as a refractory material with high thermal conductivity, good thermal shock resistance and newly available at the time of development. The columns are made up of vertical stacks of silicon carbide trays of rectangular cross-section and are commonly 760 mm wide, 1370 mm long and 165 mm deep. The top and bottom edges of the side walls of the trays are bevelled so that they fit together and are vertically aligned. Joints are sealed with a refractory cement. There is an opening in each tray placed to one side so that adjacent trays have openings at opposite sides. This allows the liquid zinc to fall from the opening of one tray onto the tray below and flow across to the opening of that tray. Zinc vapour passes upwards through the staggered openings counter to the liquid metal flow. The lower or boiler section of the column is contained within a firebrick furnace heated to a temperature of 1250°C. The upper section is cooled with a controlled air flow to partly condense zinc and provide reflux.

Two different types of tray are used. The bottom or boiler trays are termed W trays due to the shape of their cross-section, which has a deeper edge wall and peripheral trough to contain the maximum amount of zinc against the heated wall, and is illustrated in Figure 15.1. The top trays are refluxing trays and are flat bottomed and cooled to allow some zinc condensation.

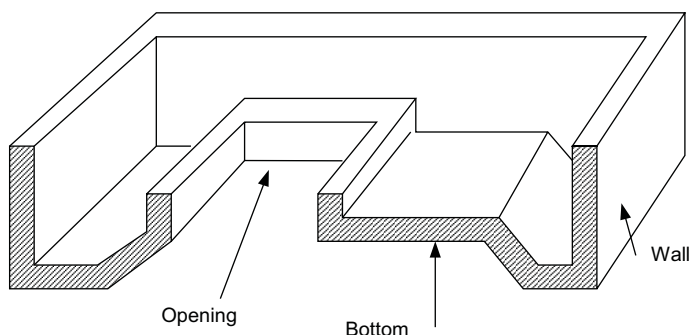


FIG 15.1 - W type boiler trays.

A schematic diagram of a distillation refining installation is shown in Figure 15.2. As shown, a refining unit generally consists of two stages in series. The first stage or 'lead column' with about 50 trays serves to separate lead and other non-volatile impurities into the bottom product, and the second stage with about 60 trays, serves to separate the more volatile cadmium as a top condenser product. The second stage or 'cadmium column' is usually made up totally of reflux trays and often two lead columns in parallel are used to feed one cadmium column.

Crude molten zinc is fed continuously at a controlled rate to the top tray of the boiler section of the 'lead column' and flows down from tray to tray against a rising stream of zinc vapour. In the reflux section, zinc vapour from the boiler section rises against a downward flow of molten zinc from condensation on the walls of the reflux trays. Residual vapour passes out the top of the column to a cooled condenser chamber constructed of silicon carbide bricks. The chamber is air cooled to condense the zinc vapour.

The bottom product from the lead column contains all the lead and iron in feed, and is run through a liquation furnace where it is cooled to 440°C to separate lead and iron. The resulting zinc is low in cadmium and generally meets Prime Western Grade specification. It may be recycled to the feed of the lead column or it may be a marketable product depending on market requirements and economics. Around half the lead column feed generally reports to the bottom product, since it is important to avoid any chance of separation of insoluble zinc-iron phases, with the potential to cause blockage of flow channels from the base of the column. Iron can also attack the silicon carbide and it is desirable to

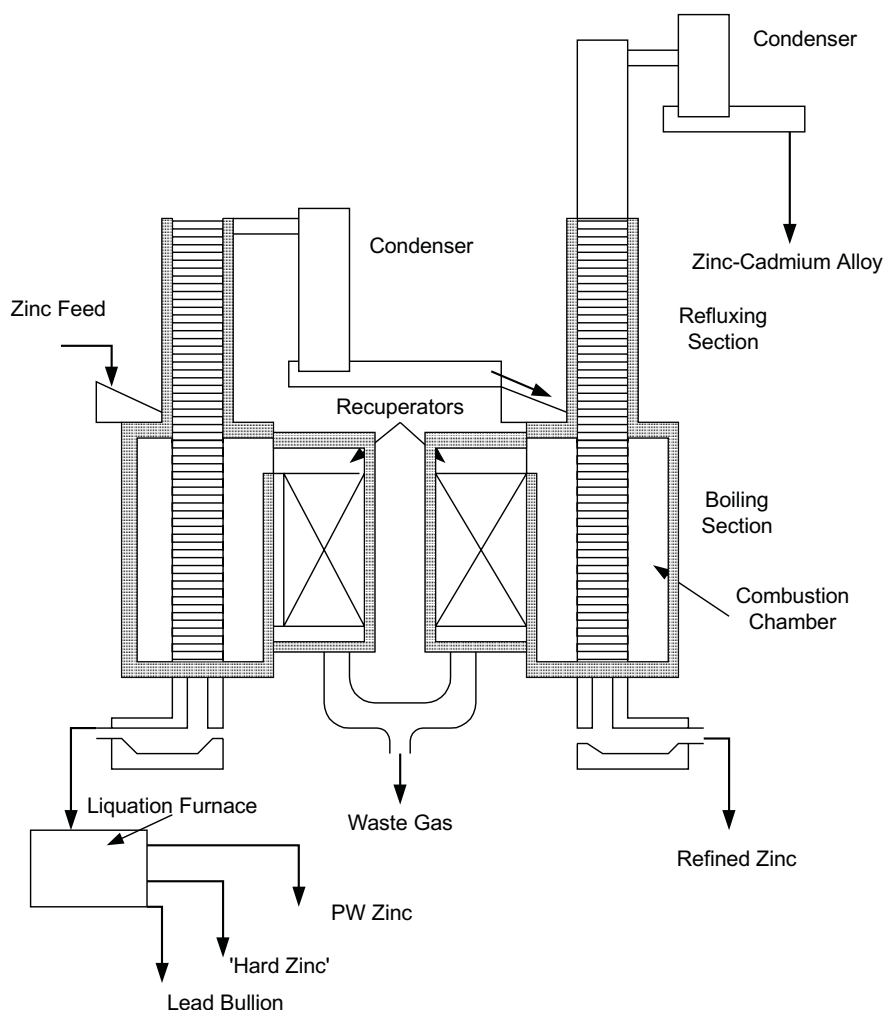


FIG 15.2 - Reflux refining unit - New Jersey Zinc design.

maintain the level of iron in zinc feed below 0.2 per cent. For trays of the common size given above, the lead column feed is of the order of 60 tonne per day and the boiling capacity is around 30 tonne of zinc per day. The other two product streams from the liquation stage are lead containing around two per cent zinc and a mixed phase termed 'hard zinc' containing around 20 per cent lead and two per cent iron.

Condensed zinc from the lead columns contains all the cadmium from the feed and flows directly into the top tray of the boiler section of the cadmium column. The bottom product from the cadmium column is high purity metal exceeding 99.995 per cent zinc, conforming to Special High Grade specifications and containing below 20 ppm cadmium. The top product is generally around 15 to 20 per cent cadmium and can be re-distilled in a separate small column to produce high purity cadmium metal and residual zinc for recycle to the cadmium column.

Few ideal theoretical stages are required to achieve the necessary separation of zinc lead and cadmium. The large number of trays used is indicative of the low mass transfer efficiency of each tray, which is generally below ten per cent (Hanko *et al*, 2000). The heat transfer surface required also determines the column size and will be the major determining factor.

The combustion chambers associated with the columns are generally natural gas fired to give a furnace chamber temperature of 1250°C. Exhaust gases pass through a recuperator to preheat combustion air to around 800°C.

The energy requirements for this process are high at six GJ per tonne of zinc (1667 kWh/tonne). In addition, the columns have limited life and must be fully reconstructed after a failure or a shutdown. It is thus normal practice to have new standby spare columns in place. High quality workmanship is an important requirement for achieving long column life.

Arsenic is a minor impurity of some significance in zinc production by carbothermic reduction due to its volatility. In the refining stage it concentrates in the bottom product of the lead column and is partly separated during liquation with iron in the 'hard zinc'. Some also remains in the zinc from the liquation bath and can be removed by sodium treatment as described earlier in this chapter.

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Zinc Fuming Processes

INTRODUCTION

Fuming generally involves the carbothermic reduction of zinc oxide to zinc metal vapour, which is then re-oxidised to a fine particulate zinc oxide or fume. The fume can then be separated from the gas stream. It is applied to the separation of zinc from low grade and complex materials, particularly secondary materials of low or negative value. Separation of zinc can be selective due to the relatively high volatility of zinc in comparison with other metals. The exceptions are lead, silver and cadmium which are usually co-recovered with zinc into oxide fumes as well as some minor impurities such as arsenic and germanium.

The direct condensation of zinc metal from vapour is preferred for the processing of high grade materials, since it avoids the need to reduce the zinc in fume a second time to produce metal. However with low-grade materials, conditions such as gas composition and dust loadings are adverse to the direct condensation operation and zinc oxide must be produced. Hence zinc is effectively separated from a low-grade material into a high grade oxide that requires further reduction to produce zinc metal. In this regard, the value of the feed must be low to be able to support the processing costs of both the fuming operation and the second stage reduction to zinc metal.

A large number of fuming processes are available to treat a range of raw material feeds. These materials can be zinc rich slags, such as from the lead blast furnace, leach residues containing zinc ferrite, oxidised zinc ores such as silicates or carbonates, which are difficult to separate by flotation methods, or dusts from the electric arc furnace processing scrap steel.

Fuming processes can also largely be divided into three broad categories:

1. Those which fume directly from solid-gas phase reactions, and include the Waelz kiln process and the shaft furnace.
2. Those which fume from a molten slag, and include the conventional slag fuming furnace and the Ausmelt submerged lance reactor.
3. Those which fume from particles in suspension in a gas stream, and includes the Flame Reactor process and the Contop cyclone reactor.

THE WAELEZ KILN PROCESS

The Waelz kiln is probably the most common process applied to the recovery of zinc from residues and secondary materials. It uses a long, refractory-lined rotary kiln similar to a cement or lime kiln. It was first patented in Canada in 1909, but was developed and applied in Germany with the first large scale plant constructed in 1925. The name of the process originated from the German 'Walzen' describing the rolling or tumbling action of material in the kiln.

Fine feed material containing oxidised zinc is mixed with carbon and fluxes as necessary, and moves slowly through the rotating-inclined kiln in countercurrent flow to a heated air stream. The carbon used is a low volatile anthracitic coal or coke fines. The charge is initially dried and preheated to reaction temperature of around 1150°C in the first part of the kiln. In the reaction zone that follows, carbon is oxidised to CO within the tumbling bed of material and the CO reduces ZnO to zinc metal vapour in accordance with the principles for carbothermic reduction as given in Chapter 11. Iron oxides are also reduced to metallic iron, which assists in the reduction of zinc and other base metal oxides. Zinc vapour is emitted from the tumbling bed into the gas space or freeboard and is immediately oxidised to a

zinc oxide fume by the excess oxygen present in the gas stream above the bed. Other volatiles including lead compounds are also carried off with the gas stream as part of the fume for subsequent collection. A diagrammatic representation of the processes taking place within the kiln is shown in Figure 16.1.

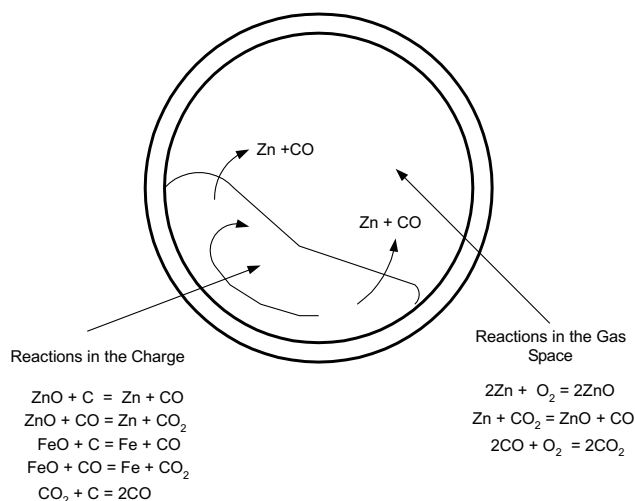


FIG 16.1 - Waelz kiln reactions.

The kiln operates with highly reducing conditions within the tumbling bed, and oxidising conditions in the gas space. The range of reactions can be quite complex particularly in relation to iron, and to the formation of molten phases such as that which has the eutectic composition $2\text{FeO} \cdot \text{SiO}_2 - \text{FeO}$, and a melting point of 1180°C . Formation of the latter material is of particular importance in accretion formation.

Sulfur is often present in the feed materials as sulfate and is reduced in the process to sulfide. This aids the separation of lead, which is mainly vapourised as a sulfide. Iron and copper sulfides can form to generate a matte phase, which can retain silver and is the reason why silver recovery into fume is relatively low for the Waelz process. Arsenic and antimony similarly may be held in the matte phases with relatively low vapourisation. Germanium and thallium however are readily vapourised as sulfides and report strongly to the fume.

Since excess carbon is maintained throughout the charge over the entire length of the kiln, low residual levels of zinc in the final solids (Waelz slag) can be achieved, particularly if extended residence times are used.

The oxidation of zinc vapour above the bed is strongly exothermic, contributing to the overall thermal balance by recovering and returning to the bed the heat lost by the endothermic reduction reactions. This is achieved through the tumbling action of the charge and transfer of heat from the kiln lining to the charge as well as by radiation. This feature of the process enhances thermal efficiency, although overall thermal efficiency of the process is relatively low per tonne of zinc recovered due to other heat losses.

It is important for the operation of a Waelz kiln that the charge maintains an open structure or 'dry condition' and tumbling action. This requires that molten phase formation should be minimised. If there is excessive melting, the intimate contact of reductant and the charge is lost and the carbon tends to become separated to the exterior of the melt, greatly lowering reaction rates. In addition, any stickiness will give rise to the formation of accretion rings on the walls of the kiln, which impede the movement of

the charge and gas through the kiln. In the extreme, this will require shutdown and cooling for accretion removal. Excess coke is commonly used as a conditioning agent to overcome these effects by adding bulk to the charge and absorbing molten phases. The quantity of coke added is normally around 25 per cent of the charge, but can be in excess of 40 per cent in some circumstances. Excessive coke can also reduce the strength of accretions and enable them to be removed from the walls of the kiln by barring down, or by changing firing conditions and using the carbon as fuel to burn them off. For this purpose the sizing of the coke is important. If it is too fine or too reactive it will burn intensively, raising the bed temperature and aggravating any charge melting problems by increasing the extent of melting and lowering the viscosity of any molten phases. If it is too coarse, then it is relatively unreactive because of the low surface area.

In order to tolerate excessive coke in the charge, it is usual to recover residual coke from the Waelz slag and recycle it to the kiln feed. It is also common practice to add some fine coal as well as coke to lower the ignition temperature of the fuel and compensate for the use of coarse coke. Fluxing materials can also be added to the charge to raise the melting point of any potential slags formed from components of the charge. Lime or limestone is commonly used for this purpose. The addition of lime also reduces the leachability of heavy metals from the slag and allows it to more readily meet environmental standards for disposal.

Performance can be indicated by the ratio $(\text{CaO} + \text{MgO}) : (\text{SiO}_2 + \text{FeO})$ in the charge and slag. At a ratio value of 0.1 to 0.2 the process works optimally. It also works well if the ratio is greater than 1.3 and poorly if the ratio is between 0.6 and 0.7 (Mattich *et al.*, 1998). These two regimes may be regarded as one of acid slags at a low lime to silica ratio, and basic slags at high lime to silica ratios.

There can be differences in the form of accretions formed under 'acid' or 'basic' regimes. With acid slags, a rise in temperature by reducing feed and increasing coke rate can be used to melt accretions. For basic slags, a drop in temperature can cause accretions to collapse, or else a change to acid conditions for a short period can remove accretions.

Since lead readily forms low melting phases such as oxide, silicates or sulfides, it cannot be tolerated in large amounts, particularly when such molten phases can separate as a pool at the base of the charge. These high lead phases can severely attack the kiln refractories. This adverse effect can be intensified by the presence of copper, forming lower melting point matte phase eutectics. For this reason, there are limits on the level of lead in the charge, which should not exceed five per cent.

The feeding of fine materials to the Waelz kiln can give rise to excessive dusting, as well as lowering the ZnO content of the Waelz oxide fume. It is therefore sometimes necessary to loosely agglomerate the feed by passing it through a drum conditioner. Otherwise recirculation of dust from the initial drop-out chamber after the kiln gas exit can capture most of the dust and significantly improve the quality of the oxide fume.

Plant Requirements and Performance

A flow sheet for a typical Waelz kiln plant is shown in Figure 16.2. The kiln is fed from a series of hoppers containing raw feed, fluxes and coke. Coke is generally an addition of at least 25 per cent of the mixed raw feed and can be up to 45 per cent depending on conditioning requirements. Coke sizing is important and is generally within the range of 2 to 6 mm with at least 60 per cent above 2 mm. Air is drawn through the kiln from the solids discharge end and is heated with an oil or gas burner. This only represents about five per cent of the total fuel requirement.

Hot gases at around 700°C leave the kiln at the feed end, pass through a dust separation chamber and then to a cooling system using a combination of air coolers and humidification towers. After cooling, the fume is separated using either electrostatic precipitators or a bag house. The gas is then vented to atmosphere. Bag filters are often preferred, but require gas cooling to below 200°C.

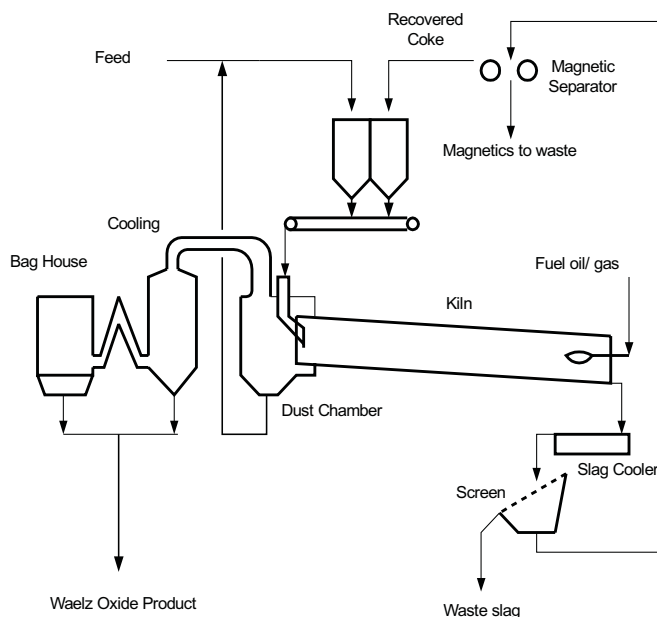


FIG 16.2 - Schematic of the Waelz kiln fuming process.

Residue or Waelz slag discharged from the kiln at around 900°C is cooled with water sprays then screened at 25 mm. The coarse lump is sent to waste and the screen fines are magnetically separated. The magnetic fraction is sent to waste and the non-magnetic fraction, which is predominantly residual coke, is recycled to the kiln via the coke bins. A typical kiln is around 4 m in external diameter and 60 m long. Large kilns can be up to 90 m in length and small units 30 m. The length to diameter ratio is commonly close to 16:1.

Refractory linings are commonly alumina brick or chrome magnesite brick backed by fireclay brick, and range from 150 mm thick for the smaller kilns to 250 mm thick for the larger kilns. The typical kiln would therefore have an internal diameter of 3.5 m and an internal volume of 577 m³.

The bed of material in the kiln occupies about 15 to 20 per cent of the kiln volume, and the time of passage through the kiln is typically five hours but can vary from three to ten hours. Rotational speed is close to one rev/min but is better defined in terms of a peripheral speed of around 10 m/min. This gives a rotational speed of 0.8 rev/min for a 4 m diameter kiln, and 1.06 rev/min for a 3 m diameter kiln. Kiln slope is in the range of two to four per cent but is typically three per cent. Both slope and rotational speed will affect time of passage. This may be approximately expressed by Equation 16.1.

$$\text{Time of passage (minutes)} = \frac{42 \cdot L}{D \cdot N \cdot S} \quad (16.1)$$

where:

- L = Kiln length in m
- D = Internal diameter in m
- N = Rotational speed in rev/min
- S = Kiln slope as a percentage

Kiln capacity can be defined in terms of raw feed throughput or in terms of metal volatilisation. General specific capacity rates are:

- 1.0 tonne per day of raw feed per m³ of kiln volume; and
- 0.15 tonne per day of zinc plus lead in fume per m³ of kiln volume.

A first order estimate of kiln volume can be made by taking the greatest of the two kiln volumes calculated from each of the above criteria. For low grade feeds the first criteria of raw feed throughput will be determining and for higher-grade materials, metal volatilisation rates will be determining. It is common practice to have a blocking ring of refractory at the solids discharge end of the kiln to bank up the charge and increase residence time. This tends to stabilise the operation in terms of steady consistent performance and reduce residual metals in slag.

Refractory life is a particular issue and generally is of the order of 12 months with about 67 per cent replacement necessary and requiring a shutdown time of around four weeks. The most severe wear on refractories takes place at the discharge end of the kiln.

Waelz Slag

The slag discharge is cooled by a range of methods, but commonly by using water sprays over a conveyor carrying the hot discharge from the kiln.

The slag generally contains around two per cent Zn or less, and 0.2 to 0.4 per cent Pb, but lower levels can be achieved with longer than standard residence times. The residual carbon or coke content can vary considerably up to 30 per cent, but may be normally of the order of 15 per cent. Two thirds of this or more may be recovered by magnetic separation as the non-magnetic fraction. Most operations process high iron content feeds and produce slags of around 30 to 35 per cent Fe. A significant proportion of this is in metallic form and hence is readily removed by magnetic separation. Lime and silica contents vary according to the type of slag regime operated, as indicated above.

Waelz slags generally appear to meet leaching criteria for environmental disposal (TCLP Test), and in this sense the process is useful for de-toxifying wastes contaminated with base metals.

Waelz Oxide Fume

Fume collected from Waelz kiln gases are predominantly a mix of zinc and lead oxides, with the zinc content generally between 58 and 65 per cent. Lead can be present also as lead sulfate or a basic lead sulfate. The crude fume will also contain some fine dust carried over from the kiln, which has passed the first fallout chamber. The presence of other minor volatile elements may be assessed from typical deportments listed in Table 16.1

Treatment of Crude Waelz Oxide

The crude Waelz oxide is of low bulk density and often contains levels of halides that are too high for subsequent processing. To address this it is common practice to further process the crude fume to remove halides (and sometimes lead), and to densify or 'clinker' the material. This can be done by heating in a second kiln to temperatures of around 850°C.

TABLE 16.1

Deportment of volatile elements to Waelz fume (Mattich et al, 1998).

Element	Recovery to Fume
Antimony	30 %
Arsenic	25 %
Cadmium	97 %
Chlorine	90 %
Fluorine	80 %
Gallium	10 %
Germanium	33 %
Indium	80 %
Silver	10 %
Thallium	80 %

Other methods involve halide removal by leaching, followed by briquetting of the dehalogenated fume. If briquetting is used to provide a feed for an Imperial Smelting Furnace, then relatively strong briquettes are required and a hot briquetting process is favoured.

The clinkering kiln is much smaller than the Waelz kiln at around 15 to 20 per cent of the volumetric capacity. Throughput is around 1.8 tonne of raw fume per day per m³ of kiln volume. The kiln is fired with fuel oil or gas only and no fluxes or coke are added to the fume. Fuel requirements are of the order of 3000 MJ per tonne of fume treated. Kiln lining is alumina or magnesia brick.

Chlorine removal varies considerably between different operations depending on application of the final product, but can be in excess of 90 per cent and fluorine removal higher at 95 per cent or more. A fume is produced and recovered from the clinkering operation and is often termed a 'lead-cadmium concentrate'. Composition can be in the range of (15 to 40) per cent Pb, (five to 20) per cent Zn, (0.5 to two) per cent Cd, and (ten to 25) per cent Cl, but depends very much on the composition of the Waelz kiln feed and raw oxide fume.

In some instances, the crude Waelz fume can be leached with a sodium carbonate solution to extract halides without dissolving zinc. The washed fume may then be used as direct feed to an electrolytic zinc plant or may be briquetted as feed to an ISF. There is also advantage in clinkering prior to washing, to reduce both lead levels and halides to the maximum extent. This is of particular benefit if the product is to be used as feed to an electrolytic plant.

Hot briquetting usually applies a roll press to fine material heated to 450°C. This may be product from the clinkering kiln, which is usually screened first to remove lump 'clinker' and the hot fines are then briquetted. A schematic flow sheet of a hot briquetting plant is given in Figure 16.3.

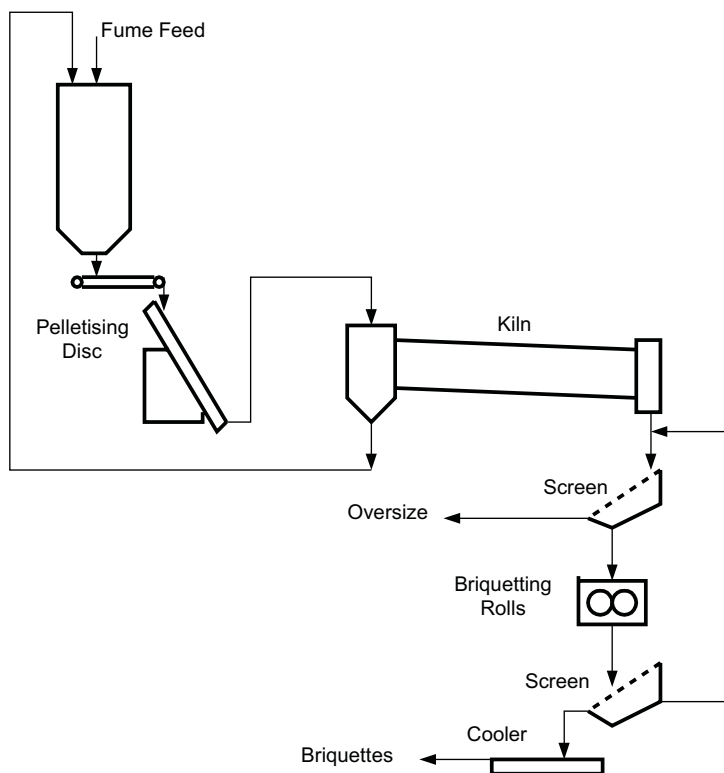


FIG 16.3 – Flow sheet for a hot briquetting plant.

THE CONVENTIONAL SLAG FUMING FURNACE

The slag fuming furnace was primarily developed for the recovery of zinc from lead blast furnace slags, with composition represented within the system SiO_2 , FeO , CaO , Al_2O_3 , ZnO . The maximum level of zinc in such slags is generally around 18 per cent by weight representing a practical solubility limit of ZnO at usual operating temperatures of around 1200°C , but varies with slag composition.

Using carbothermic reduction principles as outlined in Chapter 11 (particularly under Reduction of Molten Slags), it is practical to reduce ZnO dissolved in the slag to zinc metal, which is vapourised from the melt and swept out with reduction gases. The zinc is then oxidised back to ZnO above the slag bath by secondary air injection to form a fine particulate fume, which is collected by filtration of the gas stream. Reduction is achieved by injection of carbon into the slag bath with air. Oxygen in the air combines with carbon to form CO and generates heat to maintain slag bath temperature. As discussed in Chapter 11, there has been conjecture about the mechanism of reduction, but it is most likely controlled by kinetics and mass transfer rather than chemical equilibrium, and hence furnace performance depends to some extent on many physical factors related to the injection of coal into the slag bath and to the properties of the slag, such as viscosity.

These furnaces were developed for the recovery of zinc from lead blast furnace slags, which typically contained between ten and 18 per cent Zn and around 2.5 per cent Pb, 30 per cent FeO , 25 per cent SiO_2 and ten per cent CaO . Zinc recovery is economic only at high levels of zinc in slag, and hence slag fuming furnaces are now only applied where the zinc content of slag is at the upper end of the range at around 16 per cent or more. In fact, when such a facility is in place it benefits the lead smelter to source concentrates containing zinc in order to optimise the levels in slag. No payment is required for such zinc content and it is 'free metal' to the lead smelter.

The first commercial installation of the standard slag fuming furnace was at the East Helena lead smelter in Montana in 1927. This furnace design has subsequently been applied at a number of other major lead smelters. Copper smelter slags rich in zinc are also processed in conventional slag fumers such as at Boliden's Rönnskär smelter in Sweden, and at the Flin Flon smelter of Hudson Bay Mining and Smelting Company.

The standard furnace is constructed as a long narrow rectangular box of steel water-cooled panels. A row of tuyeres is fitted to each long side just above the furnace floor level so that a suspension of fine coal in air is blown into the molten slag through the tuyeres. A schematic of the slag fuming furnace is shown in Figure 16.4.

A typical furnace has cross sectional dimensions of 2.4 m wide by 6.4 m long and 6.4 m high. The walls are made of rows of water jackets, with three rows each of seven jackets making up each long side for the typical size. The floor is also made up of water cooled panels. There are three tuyeres in each lower jacket giving 21 tuyeres per side. Furnaces may vary in size with different numbers of side wall panels, but the width is usually constant and dictated by the depth of penetration of the blast from the tuyeres into the melt (Hancock, Hart and Pelton, 1970; and Ashman *et al*, 2000).

The water-cooled panels or jackets freeze a protective layer of slag on their inner surface, which can be studded to assist in adherence of slag. This form of containment rather than refractories has been chosen because of the aggressive conditions and the high turbulence and abrasive nature of the bath, and has been highly successful with jacket life well over ten years and up to 20 years. The price of this form of containment is the additional fuel required to compensate for the relatively high heat loss through the jackets to maintain the protective slag layer. Water is circulated through the jackets and is flashed to low-pressure steam.

Furnaces are normally operated in a batch mode and the typical size with a 15.4 m^2 cross section will hold approximately 45 to 50 tonne of slag. Slag is charged as molten blast furnace slag using a ladle and

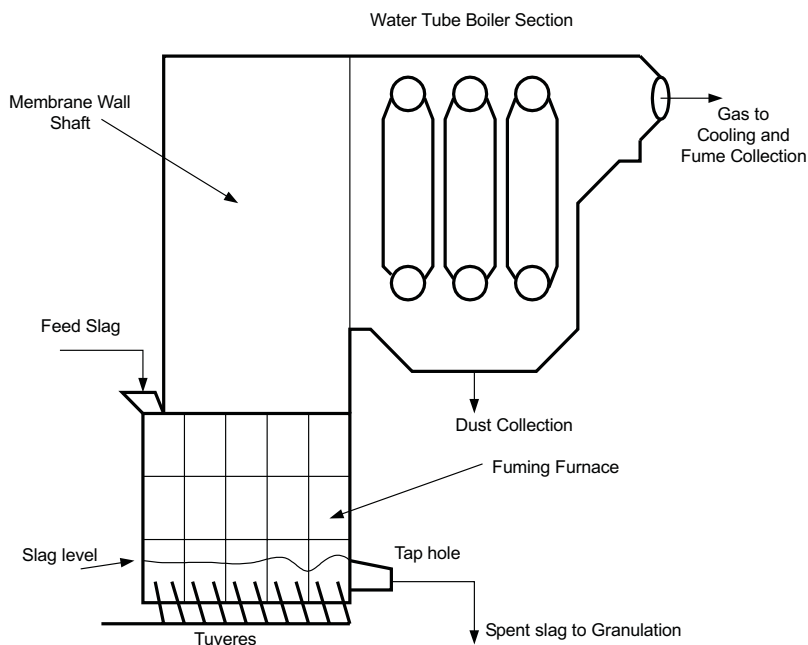


FIG 16.4 - Conventional slag fuming furnace.

also as cold slag or as residues containing zinc. In the first part of the batch cycle, air and pulverised coal are blown into the furnace to fully melt the bath and to raise the temperature of the contents to around 1250°C. The air rate for this part of the cycle is set to provide sufficient oxygen for complete combustion of coal and maximum heat generation. Some fuming of zinc occurs, but at a rate about one third of the rate under reducing conditions. The time taken for the heating phase depends on the proportion of cold material charged and the temperature of the molten slag feed.

The second phase of the cycle is the fuming phase in which the coal rate is increased, but the air rate is reduced to ensure that the oxygen supply is sufficient for 60 to 70 per cent of complete combustion. Fuming is completed when the zinc content of the slag is reduced to between two to three per cent and the furnace is then tapped to complete the cycle. Bath temperature falls during fuming but rises at the end of the cycle and can be purposely raised at the end of the batch by raising the air rate to assist in furnace tapping by lowering slag viscosity and hence reduce the time required for tapping. Alternatively, lowering the coal addition rate for a fixed air rate at the end of the cycle will also allow complete combustion to CO₂ and will raise the slag temperature in preparation for tapping.

As detailed in Chapter 11 the rate of reduction is influenced by the FeO content of the slag, which acts as a reduction catalyst. During the initial heating-oxidation stage of a batch slag fuming process, the ferric:ferrous iron ratio increases significantly and can lead to magnetite formation that precipitates from the slag raising slag viscosity. Any ferric iron must be reduced in the first part of the 'fuming' phase before significant zinc fuming rates can be achieved, and thus acts as a buffer that limits the initial rate of zinc reduction. Overall cycle times are generally of the order of two to three hours, giving an effective fuming rate within the range of 200 to 280 kg of zinc per hour per m² of furnace cross section.

A typical metal elimination curve is given in Figure 16.5, showing the zinc concentration in the slag bath with time. This relates to the fuming phase of a cycle only, from an initial slag composition 17 per cent Zn. If an initial heating phase is used then some fuming will occur during this part of the cycle at lower rates. Fuming rates may be taken from Figure 16.5 and expressed as per cent decline in zinc content per hour. This is shown in Figure 16.6.

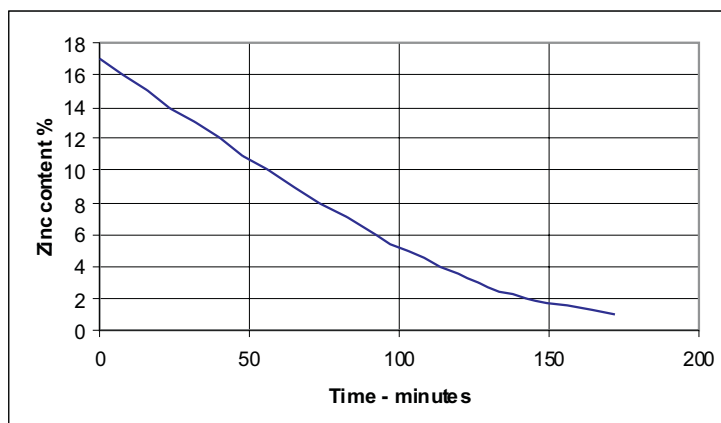


FIG 16.5 - Typical zinc in slag reduction during fuming.

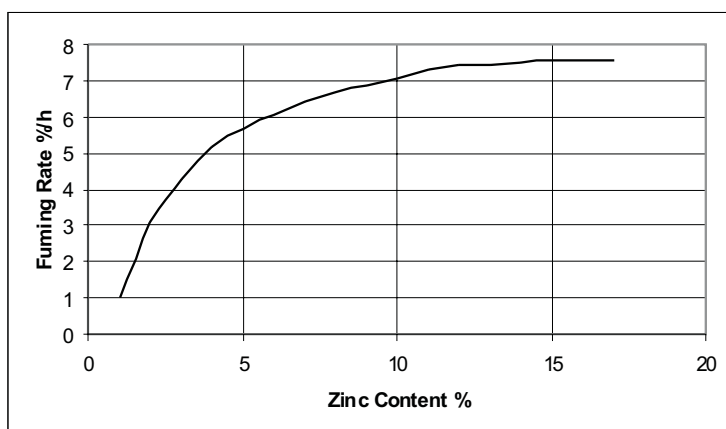


FIG 16.6 - Typical zinc fuming rate vs slag composition.

For a furnace with a 50 tonne initial charge the corresponding fuming rates in tonnes of zinc per hour are shown in Figure 16.7 as a function of furnace slag composition.

Two curves are given in Figure 16.7; the lower curve representing the instantaneous fuming rate at the particular slag composition during the cycle, and the upper curve representing the overall average fuming rate to that particular tail end slag composition. As illustrated, the rate declines significantly as fuming proceeds and the zinc content of slag is reduced.

For a total cycle, including time allowances for charging and heating and for tapping of the furnace, the tonnes of zinc fumed will be averaged over an extended time period, only part of which will cover high fuming rates. By way of example, for a total cycle including 30 minutes for furnace charging and 15 minutes for tapping, the overall average zinc fuming rate as a function of final tail slag composition is shown in Figure 16.8. The curve is relatively flat with little difference is overall furnace capacity when operating between three and nine per cent residual zinc in slag from a feed of 17 per cent zinc. However, zinc recovery is maximised at the lower residual zinc level and it is common practice to operate at a tail slag composition of around 2.5 to three per cent zinc. Below this there will be a significant fall-off in furnace capacity.

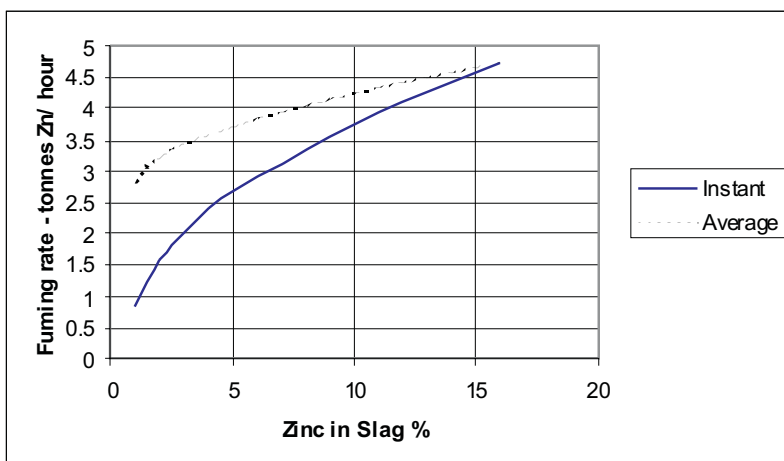


FIG 16.7 - Zinc fuming rate vs slag composition (50 tonne capacity furnace).

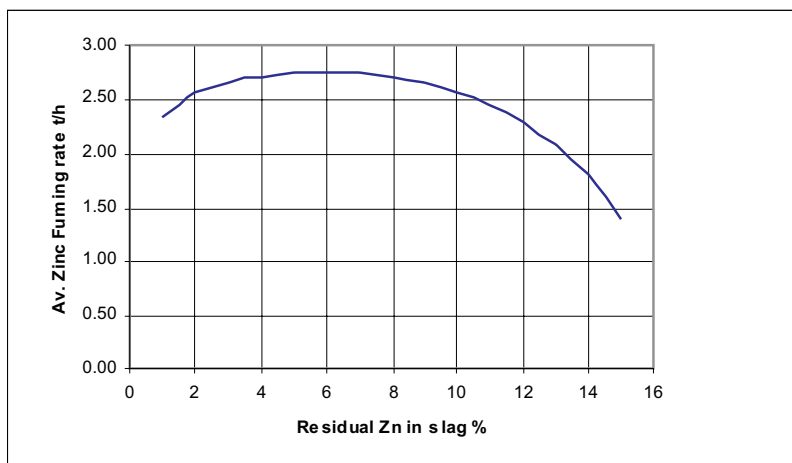


FIG 16.8 - Average overall fuming rate vs tail slag composition (50 tonne capacity furnace – batch operation).

If the fuming furnace can be charged with hot slag, then the average fuming rates over the total cycle can be increased by eliminating the heating phase. An electric slag holding furnace may be used for this purpose and indeed Cominco's Trail smelter feeds hot slag directly at 1340°C from an electric furnace associated with its Kivcet lead smelter (Ashman *et al*, 2000). In the situation with hot slag feed, the optimum tail slag composition can be lower and Cominco operate to a tail slag of close to 2.0 per cent.

Zinc is vapourised from the slag bath as zinc metal but is oxidised above the bath by the introduction of secondary air, which also burns CO to CO₂ and any fine coal particles in suspension in gas emitted from the bath. Secondary air is controlled to achieve an oxygen level of five per cent in furnace flue gas. As a result, the temperature of furnace gases above the bath can rise to 1400°C. The furnace gases pass up through a shaft composed of a water-cooled membrane wall, to a water tube boiler where the temperature is reduced to around 650°C. The membrane wall is integrated within the boiler system. Accumulation of dust on the boiler tubes and walls is a significant problem and soot blowing is extensively required usually using saturated steam.

Gases from the boiler are further cooled to below 200°C and are filtered using bag filters to capture the zinc oxide fume. Gas cooling is commonly by air coolers and by humidification in water spray towers. Air cooling by exchange with furnace combustion air to achieve a pre-heat of up to 600°C is a useful way to improve thermal efficiency and reduce coal consumption. However, in the total gas handling system there are major issues with the accumulation of sticky dust deposits and the need for constant cleaning of heat exchange surfaces and ducts to prevent flow restriction. Typical plant availability is 88 per cent and is largely dictated by the need for cleaning parts of the gas train, rather than the fuming section. Downtime can vary significantly and is critically dependent on the design of the gas handling system.

Coal is usually pulverised to 90 per cent minus 200 mesh and is transported in a fluidised state using cold air to the tuyeres, where it is injected with blast air into the slag bath. Coal consumption is of the order of 16 to 25 per cent of the slag charge containing around 17 per cent Zn and represents between 1.1 and 1.7 tonne of coal per tonne of zinc recovered. The lower end of this range requires full pre-heating of blast air, but variations also depend on the extent of charge heating required and the proportion of cold feed, as well as the length of the fuming cycle.

The presence of hydrocarbons should theoretically increase zinc fuming rates. However, in practice, coal consumption is found to be proportional to the fixed carbon content with little effect from the volatile content. This is said to be due to slower reaction rates of volatiles, which tend to burn above the slag bath (Yurko, 1970). Ash from coal dissolves in the slag and dilutes the zinc content. This tends to reduce zinc recovery and hence low ash coals generally give higher zinc recovery.

Apart from zinc, lead will fume efficiently, particularly if some sulfur is present in the slag. A slag containing 2.5 per cent Pb will be reduced to less than 0.05 per cent with a lead recovery in excess of 98 per cent. Lead is fumed ahead of zinc during the first part of the cycle. Cadmium, halides, arsenic and silver will also be fumed with high recovery. Germanium, indium, thallium, antimony and tin are fumed to varying degrees.

Operation of slag fuming furnaces in a continuous rather than batch mode has been practised, but is not common. A notable exception was at the Non-ferrous Metallurgical Works at Plovdiv in Bulgaria. If operated continuously, the composition of the slag in the furnace must be that of the tail slag. Since fuming rates reduce as the zinc content falls the fuming rate for continuous operation will be at the minimum. The reduced fuming rate needs to be offset by the time eliminated from the cycle for charging, heating and batch tapping. The initial experience with the Plovdiv plant has shown reduced capacity with continuous operation, but each case needs to be evaluated for its particular circumstances. Details of operating conventional slag fuming furnaces are given in Table 16.2.

There are opportunities to increase fuming rates for a continuously operated furnace by dividing it into a series of compartments with progressively lower levels of zinc in each. However, the general conclusion appears to have been that the best capacity is achieved by batch operation.

SUBMERGED LANCE SLAG FUMING

As an alternative to the conventional slag fuming furnace, a submerged lance slag bath reactor may be used for zinc fuming. In this process, fuel as gas, oil or pulverised coal is injected with oxygen enriched air through a vertical submerged lance into a molten slag bath contained in a refractory lined vertical cylindrical vessel. The high degree of turbulence generated by the injected gas promotes reaction rates and heat transfer.

The principles of the submerged lance rely on the cooling effects of the injected air passing down through the lance to freeze a protective layer of slag on its outer surface. Otherwise, the lance would be rapidly consumed at the operating temperature of around 1300°C. These principles were developed by

TABLE 16.2*Representative conventional slag fuming furnaces (Blanks and Ward, 1968).*

Plant	Chihuahua	Chimkent	Flin Flon	Plovdiv	Port Pirie	Ronnskar	Trail
Company	Asarco	Kazakhstan	Hudson Bay	Dimitar Blagoev	Zinifex	Boliden	Teck Cominco
Year commissioned	1952	1974	1952	1970	1966	1964	1998
Number of furnaces	1	1	2	1	2	1	1
Operation	Batch	Batch	Batch	Continuous	Batch	Batch	Batch
Length × width (m)	6.4*2.44	8.48*2.41	6.4*2.44	2.3*2.54	4.57*2.44	8.1*2.4	6.4*2.44
Height (m)	7.32	7.2	7.32		6.25	9.00	
Hearth area (m ²)	15.61	20.45	15.61	5.85	11.15	19.4	15.61
Tuyeres per side	14	14	21	11	15	26	21
Slag charge (t)	39	120	72-75	25 @ 13t/h	40-45	105	70-85
Slag - Zn%	11.7%	11-17%	8-10%	12.5-14%	16-18%	9.5%	16-18%
Slag -CaO/SiO ₂	0.88	0.7-0.8	0.047	0.61	0.7	1.33	0.61
Slag depth (m)	1.02	1.5	1.2-1.3	1.1	0.97-1.09	1.44	1.13-1.36
Tail slag - Zn%	1.9%	1.9%	0.7-1.0%	2.0-2.5%	2.2%	1.0%	2.5%
Cycle time (min)	80	130-150	180		110-200	120	150-180
Slag rate (t/day)	646	1100	560	312	380	1200	650
Fuel type	Coal	Nat. gas	Coal	Oil	Coal	Coal	Coal
Fuel use t/t zinc			2.1-2.3	1.56	1.06-1.10	2.8	
Productivity tZn per m ² day	4.05	6.50	2.94	5.86	5.04	5.25	6.04

the Commonwealth Scientific and Industrial Research Organisation in Australia with early application to tin fuming in 1978. Further development of application to zinc fuming was by Ausmelt with commercial application at the Onsan Smelter of Korea Zinc and by Mitsui at the Hachinohe ISF smelter. The process has also been applied to lead and copper smelting by Mount Isa Mines (Isasmelt Process). One key part of these processes is the design of the lance to achieve stable operation and long life (Floyd and Swayn, 1998). A schematic of the submerged lance slag bath process is shown in Figure 16.9.

Feed materials together with fluxes and lump coal are directly fed into the bath through a port in the reactor lid. Fuel is injected with air enriched to up to 35 per cent oxygen, into the bath through a lance which is supported on a hoist so that it can be lowered into the bath and raised free of the reactor for cleaning or replacement. The need to have an adequate volume of gas flowing through the lance to provide cooling, limits the degree of oxygen enrichment possible. Secondary or after-burning air also is supplied through the lance assembly but exits from the lance above the bath level. Additional secondary air enters through the feed and lance ports, but these are normally as constricted as possible to limit this uncontrolled input. The vessel is maintained under slight suction from the gas handling system. The slag bath is highly turbulent and the reactor vessel needs to be tall (at about three times the vessel diameter) to prevent splashing of slag into the gas outlet duct, which can cause blockages. Since the lance needs to be fully withdrawn from the reactor, this requires a relatively high structure to accommodate the plant.

Secondary combustion can generate elevated temperatures in the gas above the bath, and requires cooling before the fume is separated. As shown in Figure 16.9, gas is cooled firstly in a waste heat boiler consisting of a membrane wall shaft to drop the temperature to below the point where fume is sticky,

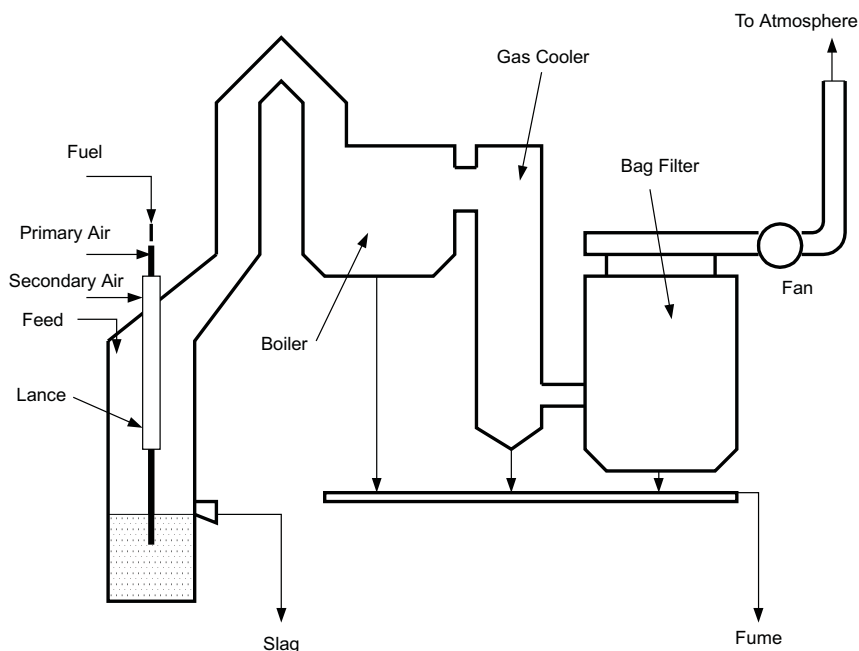


FIG 16.9 - Schematic of submerged lance slag bath reactor.

followed by a water tube section. Additional cooling is by humidification using water sprays to drop the temperature below 200°C so that fume can then be collected using bag filters. For a small plant, the cost of a boiler may not be justified and cooling by humidification alone can be used. Collection of fume using an electrostatic precipitator is also practical and will allow collection at a higher temperature than a bag filter (400 – 500°C), thus limiting the degree of cooling required. If an electrostatic precipitator is used, it should contain at least three fields in series to ensure efficient removal of fume to low levels. To ensure that fume is removed and exhaust gas meets environmental standards, the use of a bag filter often has been preferred.

The gas handling and fume collection facilities are essentially the same as for the conventional slag fuming furnace as discussed earlier in this chapter, although in this case it is possible to significantly reduce the volume of furnace gases by a higher degree of oxygen enrichment and because of the possibilities of having a much more gas tight system, with fewer opportunities for air ingress.

Slag Bath Reactor Operating Principles and Construction

The chemical principles are the same as those described for the conventional slag fuming furnace and fuming rates are of a similar order. However, it is usually preferable to operate the slag bath reactor continuously rather than in batch mode. This can avoid the need for feed slag holding facilities and larger gas handling volume capacity, which is the primary cost of the plant. The cost of the reactor is relatively small in comparison with the conventional fuming furnace and extended residence time can be more readily accommodated.

Zinc is fumed from molten slag as metal vapour and is oxidised to ZnO fume above the bath by secondary air. Considerable heat is generated by secondary combustion, and can be partly captured by the bath as molten slag is projected into the gas space by the turbulence generated by the lance. This heat capture by the bath reduces the actual fuel needs within the bath and improves fuel efficiency.

The high level of turbulence is in the centre of the reactor around the lance and well away from the reactor wall, unlike the conventional slag fuming furnace where injection tuyeres are located in the furnace wall and gas can rise along the wall. In the case of the conventional furnace, refractory lining of the furnace walls is not possible and the water jacket containment design is necessary. For the submerged lance reactor, refractory lining is possible but even so there is sufficient turbulence to severely impact on refractory life. In some installations, refractory life was less than three months with plant availability under 80 per cent. However, this has generally improved with experience and refractory life exceeding two years can be achieved using chrome magnesite fused grain re-bonded bricks for typical iron silica slags. Backing the refractory layer with water cooled panels can also assist in increasing refractory life.

The use of a water jacketed system alone places a limit on the operating temperature, which cannot be much above the liquidus temperature of the slag. This limitation can be relaxed with refractory lining provided critical temperatures for degradation of the bricks are not exceeded. With the use of water jackets, the formation of metallic iron during fuming must be avoided. This will limit the reducing conditions that can be applied, and the final level of zinc in tail slag should be above two per cent. This is not so critical for the refractory lined reactor and final slags of one per cent Zn or below are practical. The selection of the final zinc content of slag will be determined largely by fuming rate considerations, but increased temperature can assist in comparison with the conventional furnace. Although the risk to the integrity of the furnace associated with iron formation is reduced with refractory lining, it does need to be avoided over long periods of operation since it will give rise to severe accretion formation and blockage of the furnace.

Figure 16.10 illustrates the effect of reducing conditions as indicated by the final level of zinc in slag, on the formation of metallic iron. This data relates to the fuming of ISF slag and shows the combustion stoichiometry required to avoid metallic iron formation.

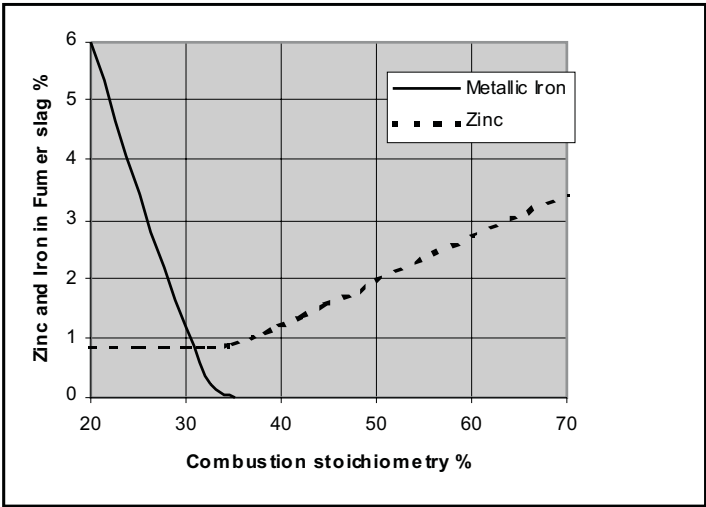


FIG 16.10 - Metallic iron and zinc content of slags vs reducing conditions (Sekiguchi and Azuma, 1998).

Due to the heat developed by secondary combustion of zinc vapour and CO above the bath, high gas temperatures can be developed in the upper section of the reactor. This can also affect refractories by exceeding their critical breakdown temperature. In this situation, the use of a water cooled wall has benefits, particularly as loss of heat at this point assists in gas cooling. Following these principles, Korea Zinc has proposed the use of cooling water circulating through copper sets within the refractory

in the lower part of the reactor and in contact with the slag bath, and a water cooled membrane wall with frozen slag layer protection for the upper section (Kim and Lee, 2000; and Mounsey and Piret, 2000). These questions of containment and refractory life are the primary concerns in the application of this process and are still in an evolutionary phase at the time of writing. Otherwise, the approach has the advantage of relative simplicity.

With operation in a continuous mode, it is practical to use multiple stages in series with slag flowing from one reactor to another. This can increase the overall fuming rate for a given reactor volume but also is useful to separate gas streams if the feed material contains sulfur. The first stage can be used to eliminate sulfur as well as fuming zinc and lead, and the second stage can complete slag fuming to low levels of residual zinc. This approach is useful for the processing of leach residues from an electrolytic zinc plant. It also has the potential to process low-grade complex ores or concentrates, which are difficult to separate by conventional mineral dressing methods (Buckett and Sinclair, 1998).

The handling of sulfur bearing gas will depend on the concentration of SO_2 . If derived from the direct fuming of sulfide feeds it will be high, and can be handled in a standard contact acid plant after separation of fume and scrubbing. If the SO_2 concentration is low, the gas may be scrubbed with a lime suspension or alkaline solutions. Alternatively, zinc oxide fume can be used in a water suspension as a scrubbing medium, to absorb SO_2 and form zinc sulfate. If part of a conventional electrolytic plant, the zinc sulfate can be directly added to the hydrometallurgical circuit or it can be injected into the roasters for decomposition back to ZnO and SO_3/SO_2 for eventual conversion to sulfuric acid. When operated as two stages in series, the composition of the fumes from each stage will be significantly different with higher levels of lead and silver in the first stage fume.

When operated in batch mode, fuming rates for the submerged lance slag bath reactor are comparable with average rates achieved in the batch operated conventional fuming furnace as detailed earlier in this chapter. This gives an indicative average decline in zinc content of six per cent per hour between 17 and three per cent zinc content. From Figure 16.6 the continuous fuming rate at a slag composition of two per cent zinc is equivalent to around four per cent decline in zinc content per hour. For a reactor containing 1 m slag depth, the slag contained is approximately 3 t/m^2 of cross section and the zinc depletion rate is thus of the order of 0.12 t of zinc fumed per hour per m^2 of furnace cross section. This represents a crude indication of reactor capacity only, as gas flow rates are also a major determining parameter and can differ significantly from the conventional slag fumer in relation to bath cross-sectional area.

HIGH INTENSITY FUMING PROCESSES

These processes generally involve the injection of zinc containing material into a high temperature reducing flame. Zinc oxide is reduced to zinc metal vapour reporting to the gas stream. Slag as a suspension in the gas stream is separated either in a settling or impingement chamber or in a cyclone. Secondary air is added to the gas stream after slag separation to burn CO to CO_2 and zinc vapour is oxidised to form zinc oxide fume, which is separated by gas filtration. Principles are the same as described above for other fuming processes, with the exception that the reduction step is conducted at high temperatures, with very high reaction rates and hence small equipment volumes. High levels of oxygen enrichment are also used so that gas volumes and subsequent gas handling equipment size is considerably reduced.

A number of variants of this approach have been proposed and evaluated but there are no full scale commercial operations solely for the purpose of zinc recovery. Two processes closest to commercial development for zinc applications are the Horsehead Flame Reactor and the Contop Flame Cyclone Reactor.

Horsehead Flame Reactor (Bounds and Pusateri, 1990)

This process was developed by Horsehead Resource Development Company Inc. in the USA for the processing of electric arc furnace (EAF) dusts from the processing of steel scrap, and containing between ten and 35 per cent zinc. The objective was to develop a technology that would be viable at a small scale and suitable for installation at steel plants producing EAF dusts. The slag could be returned to the steel process and the zinc oxide fume sold to a zinc smelter.

Initial reactor designs were based on the use of pulverised coal as the fuel but later extended to the use of natural gas. Natural gas performs better due to more rapid combustion rates and higher achievable temperatures. Higher temperatures enable molten slags to be produced from most feed materials without flux additions. A schematic of the Flame Reactor process is shown in Figure 16.11.

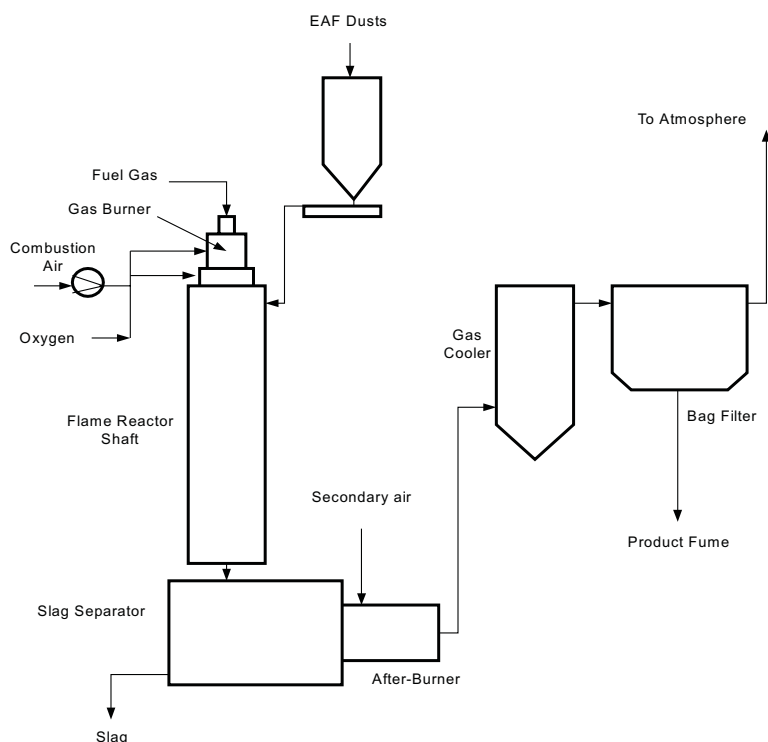


FIG 16.11 - Horsehead flame reactor.

Natural gas is burned in oxygen enriched air at 40 to 80 per cent O_2 , under excess fuel or reducing conditions to give a flame temperature in excess of $2200^{\circ}C$. The burner fires vertically downwards into a water-cooled shaft. Fine dry zinc bearing material is injected with air into the flame at the top of the main shaft and just below the flame entry. At this point temperatures within the flame are 1600 to $1800^{\circ}C$. Zinc oxide is rapidly reduced and zinc metal volatilised, and the other non-volatile components fuse to form slag droplets in suspension in the gas stream. Some slag droplets will impinge on the water-cooled shaft walls and will freeze, forming a protective layer. The bulk of the slag will be swept out of the shaft and into the slag separation chamber. The swirling action of the gas tends to separate the slag onto the walls of the circular chamber, and molten slag collects in the bottom from where it is continuously tapped.

After slag separation the gas enters an after-burner where secondary air is added to burn CO to CO₂ and zinc vapour to a zinc oxide fume. Gases are then cooled and fume separated in a bag filter. There are possibilities of sending gas from the slag separator directly to a zinc condenser to recover zinc as metal instead of oxide fume, but the conditions for zinc condensation are particularly difficult.

Oxygen to natural gas volume ratios in the burner range between 1.2:1 and 1.8:1 and the adiabatic flame temperature target is 3100°C. Also it is preferred to operate with CO:CO₂ ratios of between 0.2:1 and 0.3:1 to achieve zinc recoveries in excess of 90 per cent. Zinc recovery is not highly dependent on the degree of oxygen enrichment above 50 per cent. Lead and cadmium also fume efficiently at over 99 per cent recovery from the typical EAF dust. Some slag reports to fume as carry-over particulates, and the initial performance data suggests that this represents less than five per cent of slag produced.

Natural gas consumption for the small scale reactor treating 20 000 tonne per year of EAF dusts is of the order of 10.5 GJ/ t and oxygen use of the order of 500 kg/ t. This equates to around 50 GJ of natural gas plus 2500 kg of oxygen per tonne of zinc recovered in comparison with coal use in a conventional slag fumer of 42 GJ per tonne of zinc recovered and no oxygen demand. The operating costs are thus significantly higher but the plant is much smaller and the capital cost is significantly lower than for the conventional slag fumer.

The Cyclone Flame Reactor

The cyclone flame reactor concept originated in Russia in the 1950s for the flash smelting of copper concentrates to serve as a means of dispersing fine concentrates into suspension at the top of a smelting shaft. With conversion from air to oxygen it was found that intense reactions could take place within the cyclone and the shaft could be eliminated.

The cyclone furnace is a water cooled cylindrical vessel open at the bottom. Fine dry feed is introduced at the top and oxygen is injected tangentially. Temperatures above 1700°C are reached and smelting reactions are rapid and take place within the cyclone chamber. For copper concentrates, a 1.6 m³ cyclone reactor can process 300 t/d of concentrates. The thermal load on the reactor walls is very high and evaporative cooling with generation of steam is necessary rather than circulatory water cooling as used in standard water jackets.

The technology was developed by KHD Humboldt Wedag AG in Germany and has been commercially applied mainly as a retrofit to copper reverberatory furnaces.

For application to zinc, the process has been piloted, but no commercial installations have been made. The concept is applicable to both the treatment of zinc concentrates and to zinc containing residues, as well as secondary materials, which require the addition of fuel as coal (Henrich *et al*, 1985). A pilot cyclone furnace was also applied to fuming lead blast furnace slags at the Port Pirie smelter (Blanks and Ward, 1968). A schematic of a proposed residue processing plant is shown in Figure 16.12 (Asahari, 1996).

Feed material is pre-dried, mixed with fluxes and coal, and injected into the reactor with air and oxygen. Combustion takes place rapidly and zinc is reduced and vapourised into the resulting gas stream. Molten slag collects on the walls of the cyclone furnace and runs down into a collection chamber below. Importance is given to maintaining the oxygen partial pressure in the cyclone chamber below 10⁻³ atm.

Gases also vent through the slag collection chamber where secondary air is added to burn CO and zinc vapour to form a zinc oxide fume. Gases pass up through a membrane wall shaft, through a water tube boiler to an electrostatic precipitator where fume is collected.

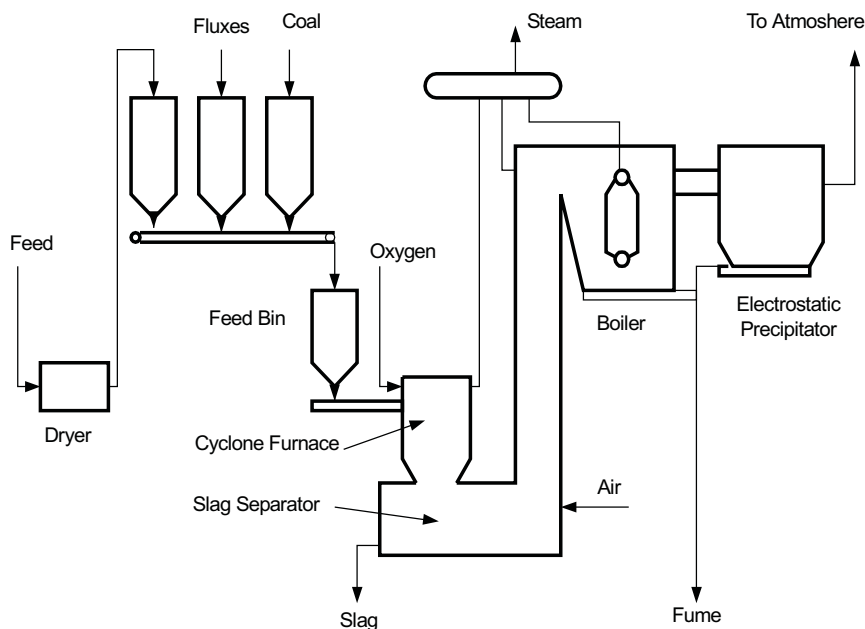


FIG 16.12 - Flame cyclone fuming process.

The general process is similar in many respects to the flame reactor and other fuming processes but with a different initial combustion device. As for the flame reactor, the use of oxygen for combustion reduces the size of gas handling equipment and hence a significant part of the capital cost of the plant.

FUMING IN THE SHAFT FURNACE

The use of a shaft furnace or blast furnace for fuming zinc involves the same principles as the ISF (Chapter 14), except that air or oxygen is introduced near the top of the furnace to complete combustion and form zinc oxide fume. It is more applicable to lower grade residues and particularly zinc ferrites.

The residue is mixed with fluxes and coal or coke fines and is pelletised or briquetted to provide lump material of suitable strength and sizing to maintain an open structure in the shaft with good gas permeability. Briquettes and lump coke are charged to the furnace. Air is blown in at the base through tuyeres as for the ISF but in this case it is practical to also inject significant amounts of fuel as oil or natural gas as a coke-saving measure.

Secondary air is injected at the top of the furnace above the surface of the charge or through a gas ring part way up the shaft. In the latter situation much of the heat generated by secondary combustion is transferred to the descending charge, enhancing fuel efficiency. However, the zinc oxide formed as a fume will tend to adhere to the charge and will not be fully recovered into the gas stream. This will establish a circulating load of zinc within the furnace, which will consume extra carbon and to some extent defeat the objective of improved fuel efficiency. The zinc oxide will also adhere to the walls of the shaft, giving rise to accretions and requiring regular cleaning.

Secondary combustion above the furnace charge significantly reduces these problems but because of the tendency to operate at lower $\text{CO}:\text{CO}_2$ ratios than the ISF, re-oxidation of zinc vapour will occur to a greater extent as the gas cools moving up the shaft. Hence accretion problems will be substantially greater than for the ISF.

The use of the shaft furnace for recovery of zinc by fuming thus incurs considerable accretion formation and requires regular shutdown for cleaning. As a result, these installations are usually small scale and can use multiple shafts on a campaign basis. The approach has generally not found favour in comparison with other processes.

A variation of the above approach was developed by the Mitsui Mining and Smelting Company at the Miike Smelter to process zinc leach residues, but subsequently changed mainly to the processing of EAF dusts. The feed materials, fluxes and coal fines are briquetted and are charged to the top of the shaft furnace as shown in Figure 16.13.

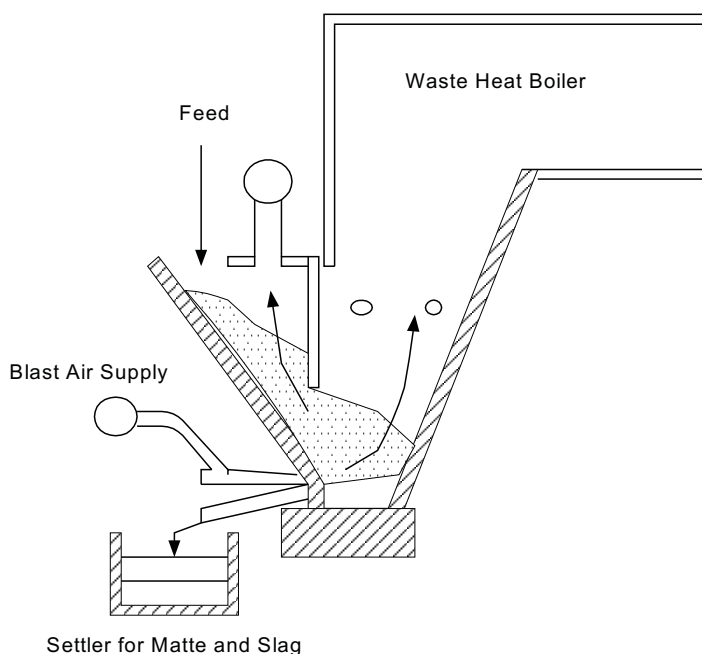


FIG 16.13 - Mitsui shaft fuming process.

The top of the furnace is maintained at an elevated temperature under reducing conditions to minimise accretion formation. Air is injected through tuyeres at the base of the furnace to generate reducing conditions and vapourise zinc and lead. Slag and matte run from the base of the furnace and are separated. Most of the gases pass through a waste heat boiler with secondary air injection to oxidise the zinc, and the gases are cooled and subsequently filtered to recover a crude zinc oxide. The zinc oxide is used as feed to either an ISF or an electrolytic zinc plant.

Typical products from combined leach residue and EAF dust treatment are reported as:

Crude zinc oxide	55% Zn, 15% Pb
Matte	50% Cu, 2000 g/t Ag
Slag	3 % Zn, 35% Fe

It is possible to treat zinc ferrite residues in a shaft furnace so as to form both pig iron from the base of the furnace and zinc fume from the top of the shaft. Some modifications of this approach have been applied on a small scale. Kawasaki Steel developed a variant of the shaft furnace that uses a circular cross section shaft charged with coke. Oxygen is injected through two sets of tuyeres at different levels.

Steel plant dusts containing zinc are blown into the furnace through separate injectors at the upper tuyere level. Iron is formed and is tapped with slag from the base of the furnace. Gases containing zinc vapour and oxide fume are simply cooled and scrubbed to recover a material containing at least 60 per cent Zn as a mixture of metallic zinc and zinc oxide.

Westinghouse operated a similar process at Hamilton, Ontario but using a plasma torch in the base of the furnace shaft to provide the heat requirements. This is similar to the SKF Plasmadust process but produces zinc oxide rather than attempting to condense zinc to metal (see Chapter 17) (Chalfant, 1996).

FUME TREATMENT

Crude zinc oxide fume produced by the various fuming processes contains a range of other volatile impurities, particularly lead and halides, but also contains fine particulate slag carried over from the fuming furnace with the gas stream. The carry-over depends to a large extent on the process used but is generally between two and five per cent of the slag produced.

The presence of other volatile elements can be significant, depending on the application of the fume and the process used for conversion to zinc metal. If the fume is to be used as feed to a retorting process or to a blast furnace (ISF) then the requirements are not so critical, other than the need for densification or briquetting. A secondary clinkering kiln or hot briquetting process is commonly used, as discussed for the Waelz kiln process in the introduction to this chapter.

If the fume is to serve as feed to an electrolytic zinc process, there is a need to remove halides, which are only tolerated in limited amounts in sulfate electrolytes, due to the detrimental effects on electrodes during electrolysis as well as the occupational health risk associated with chlorine generation from open electrolytic cells. It is therefore usual to treat fume to remove halides prior to feeding to an electrolytic zinc process. Raw fume may be washed with water to remove halides. To prevent loss of zinc and other metals into the wash solution it is usual to use sodium carbonate solution for fume washing. This converts soluble zinc and other metal chlorides and fluorides to sodium chloride or fluoride and insoluble metal carbonates, which are retained with the fume. Wash solutions are generally maintained at a pH of 9.0 to 9.2. Alternatively, the fume can be first washed with water and the resulting solution treated with sodium carbonate or caustic soda to precipitate zinc (Chabot and James, 2000).

Halides may be removed by heating the fume in a gas or oil fired rotary kiln to around 1200°C with a residence time of more than 12 hours. This can remove over 90 per cent of the chlorine content and 95 per cent of the fluorine content of raw fume. Secondary kiln treatment can also be used to remove significant amounts of lead, but higher temperatures are required. Removal is achieved by volatilisation of species such as PbCl_2 , PbF_2 , and ZnCl_2 . The hydrolysis reaction given in Equation 16.2 also takes place, the water vapour being derived from combustion of fuel.



Complex fluoro-chlorides, PbClF and ZnClF are also known to be present. In general, halogen removal improves with higher firing and exit temperatures.

Rotary kilns used for de-halogenation require a capacity of the order of 0.6 m³ per tonne of raw fume processed per day, and typical kilns are of the order of 2.0 to 2.5 m OD and 20 to 30 m in length. Kiln slope is around 4° and refractory lining is typically 150 to 250 mm thick. Examples of commercial operations are given in Table 16.3.

Kiln gases pass through cyclones to remove dusts and are then scrubbed with a sodium carbonate solution before discharge to atmosphere. Scrubbing liquor can be around 20 g/L Na_2CO_3 at a pH of 8.5. The carbonate scrubbing liquor precipitates zinc, lead and cadmium carbonates and leaves the halides

TABLE 16.3*Dehalogenation kiln installations (data provided by Grant, 2004).*

Plant Year	Company	No Kilns	Kiln		Rotation rev/min	Firing End °C	Exit Gas °C	Feed Rate t/d
			Length m	O Dia m				
Chihuahua 1952	Asarco	1	22.86	2.13	1.43	1400	650-740	100-112
El Paso	Asarco	2	18.29	2.44	1.3	1384-1440	705-755	130-140
Kellogg 1943	Bunker Hill	1	22.86	2.13	0.94-1.05	1290-1370	600-760	68-77
Ronnskar 1964	Boliden	1	39.6	2.38			700	127
Port Pirie 1966	Zinifex	2	27.5	2.44	To 2.5	1150-1200	400-650	200
Selby 1953	Asarco	1	22.86	2.13	1.3	1260		90
Tooele	Intl Smelting and Refin	1	21.34	2.13	1.1	1260	704-815	73

in solution. The collected and precipitated solids from the scrubber are separated by thickening and filtration and are returned to the kiln feed. Fuel consumption is of the order of 3000 MJ/tonne of fume processed.

Product fume from a dehalogenation kiln is usually cooled in a rotary drum cooler. The raw fume will greatly increase its bulk density and particle size, and will require grinding before feeding to a leaching operation. The presence of some impurities in the fume can influence the densification, for instance, the presence of silica derived from dust carry-over from the fuming operation can be of concern if above 0.5 per cent in raw fume as it tends to form a hard clinker, which is difficult to grind. Generally kiln processing will be more efficient in removing halides to low levels, but is more expensive than washing.

Because of the presence of particular impurities such as germanium, arsenic, antimony, indium and selenium in fume, as well as relatively high levels of lead, it is often preferable to treat the dehalogenated fume in a separate leaching circuit from the main calcine leaching circuit of an electrolytic zinc plant. This enables the impurities to be more efficiently removed in concentrated form and provides a second opportunity for leach solution purification in the main solution circuit. Lead can also be separated from a separate leach circuit as a high grade sulfate residue containing silver without dilution by gangue minerals, which would occur if the oxide fume were to be leached with calcine. At higher grades of 70 per cent or more lead, the resulting lead-silver residue will be more readily marketable to a lead smelter.

Fume is generally more difficult to leach than conventional roaster calcines and an initial weak acid leach followed by a neutral leach, or 'reverse leach' as shown in Figure 16.14, is used.

In the fume leach process outlined, ferric sulfate solution is added to the acid leach solution prior to the neutral leach to allow for removal of impurities such as arsenic, germanium and indium by co-precipitation with iron. The resulting neutral leach solution can then join the calcine neutral leach ahead of solution purification by zinc dust cementation. An additional zinc dust purification stage can be included in the fume leach circuit if needed due to heavy impurity loads – such as cadmium.

One method of selective separation of zinc oxide from a mixed oxide fume is to leach the fume with an ammonia–ammonium carbonate solution to selectively dissolve zinc as an ammine complex, leaving lead and other metals in the leach residue. Zinc may be precipitated from the leach solution as a basic zinc carbonate by stripping the ammonia from solution using steam. The basic carbonate precipitate can then be calcined at 300°C to zinc oxide at around 79 per cent Zn content (Buckett and Sinclair, 1998). This approach avoids the formation of lead sulfate from the alternative dilute sulfuric acid leach to extract zinc. The lead is in carbonate form, which can be readily reduced to metal.

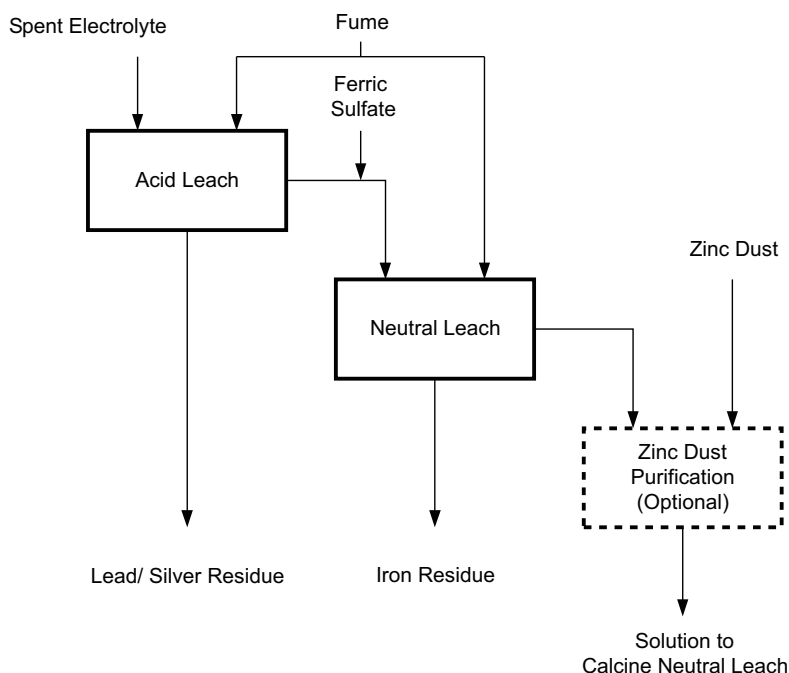


FIG 16.14 - Fume leaching circuit for incorporation into electrolytic zinc production.

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Electric Furnace Reduction Processes

ELECTRIC FURNACE TYPES

The provision of heat to a carbothermic reduction process can be made efficient using an electric furnace. The generation of process gases is minimised with associated savings in heat losses and equipment costs. This is, of course, off-set by the cost of supplying heat from electrical energy rather than fuels. In general, this approach is only economically justified if zinc is recovered as metal by condensation, rather than re-oxidation and collection as a zinc oxide fume from furnace gases. The recovery of zinc by condensation to metal requires that the furnace is gas tight to prevent the ingress of oxygen.

High temperatures can be readily achieved in the electric furnace, giving the opportunity for a broader range of slag compositions. However, this requires greater attention to methods of protection of furnace refractories.

There are three principle methods of electrical heating:

1. resistance heating,
2. induction heating, and
3. plasma or arc heating.

Of the first type, the approach used in most metallurgical applications is the electrical resistance of a molten slag bath. Electrodes are immersed in the molten slag and the current flow between them generates the necessary heat to operate the furnace. The electrothermic retort detailed in Chapter 13 is also a form of electric resistance heating furnace but for a dry rather than molten charge, in an enclosed retort.

Induction heating is used for heating a highly conductive melt and in zinc metallurgy is commonly used only for metal melting and casting operations, rather than extractive processes.

Plasma or arc furnaces supply heat from an open arc struck between two or more electrodes or between an electrode and the bath. Heat is supplied to the molten bath by convection from the hot arc gases sweeping across the surface and by radiation. This approach has become more prominent with the increasing capability of generating high voltage DC power supply.

SLAG RESISTANCE FURNACES

The standard slag resistance furnace usually uses three phase AC power with either three or six electrodes. The charge is added around the periphery of the furnace to form a bank against the walls and floating on the underlying molten slag layer, leaving an exposed molten slag surface in the centre of the furnace around the electrodes as the high temperature zone. The bank of charge provides protection for the furnace wall refractories. There may or may not be a molten metal layer or matte layer beneath the slag. The electrodes are normally submerged up to 0.5 m in the molten slag layer, but may also be held just above the surface to form a short arc between the bottom of the electrodes and the surface of the slag. In the latter situation, a large amount of heat is generated at the slag surface. A circulation pattern is set up within the slag, moving out across the surface from the electrodes towards the walls and returning below. This flow interacts with, and transfers heat to the charge layer. Power supplied to the furnace is simply expressed by Equation 17.1.

$$P = V^2/R \quad (17.1)$$

where:

P is the power input in watts

V is the voltage

R is the slag resistance

Control is achieved primarily by setting the supply voltage by changing tapplings on the supply transformer. Minor adjustments for fine control may be made by raising and lowering the electrodes to affect R . The basic positioning of the electrodes in terms of immersion depth influences the distribution of current and hence heat generation within the slag. With shallow immersion or as indicated, even positioning above the surface, heat is concentrated in the surface layer of the slag bath with increased transfer of heat to the charge banks. Deeper immersion provides greater heat input to the slag itself. The strategy used depends on the process and where the heat is required, but there is considerable flexibility and opportunity to control heat generation within the furnace.

Electrodes may be prefabricated graphite rods for smaller furnaces or Soderberg electrodes for larger furnaces. The Soderberg electrode use a paste of ground anthracite and pitch contained in a sacrificial steel tube. As this is consumed and moves into the furnace, the paste is baked and eventually graphitised in the high temperature zone when it becomes electrically conducting. A temperature of at least 1000°C is required for the electrode to become fully conducting. The supply current must therefore initially be carried by the steel casing and internal support fins, and these must be of sufficient cross-section. The operating current density of Soderberg electrodes is generally around 3 amps/cm² and the steel casing can carry up to 250 amps/cm² of cross-section. With prefabricated graphite electrodes, current densities up to 10 amps/cm² are practical, hence smaller cross sections can be used.

Power input to furnaces with Soderberg electrodes is generally within the range of 60 to 120 kW per m² of hearth area. For smaller furnaces with graphite electrodes, this can be up to 300 kW/m². The voltage-ampere rating of the furnace will be five to 15 per cent higher than the power rating in kW due to the power factor, which can be between 87 and 95 per cent. The supply voltage depends on slag conductivity and electrode spacing but is typically in the range of 75 to 250 volts. Electrical conductivities for some slags are given in Table 17.1.

TABLE 17.1
Electrical conductivities of typical slags (Shizkov et al, 1959).

Slag Composition (wt %)				Specific conductance (ohm ⁻¹ cm ⁻¹)	
SiO ₂	CaO	FeO	ZnO	1200°C	1300°C
48	30	22	0	0.38	0.70
48	30	17	5	0.24	0.46
40	40	20	0	0.90	1.40
30	36	34	0	0.75	1.40

The configuration of furnaces is usually rectangular with in line electrodes for large capacity units, and circular for smaller units with three electrodes arranged in a triangular pattern. The inter-electrode spacing distance is set by process requirements and slag conductivity, but is commonly in the range of 2.8 to 3.2 D for furnaces with Soderberg electrodes, where D is the electrode diameter. A similar spacing from the electrodes to the walls is used. On the basis of an average 3 D spacing the dimensions of standard furnaces is shown in Figure 17.1. The circular furnace may be somewhat more compact with 2.8 D inter-electrode spacing and a furnace internal diameter of 8.8 D.

Furnace heat losses are of the order of 2 kW/m² for the walls and 5 kW/m² for the floor when there is a conductive molten metal layer such as lead or iron. A heat balance given heats of reaction, heat losses in slags and gases, heat losses through the furnace and the heat content of input materials, will enable the electrical energy input to be calculated for any particular duty.

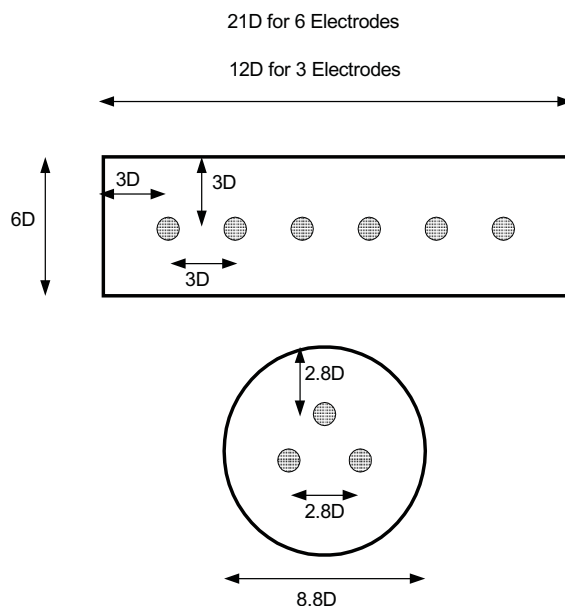


FIG 17.1 - Standard furnace dimensions (Soderberg electrodes).

Furnaces are often constructed of a water cooled steel shell lined with refractory brick (commonly chrome-magnesite for lead and zinc applications). Design must allow for significant amounts of thermal expansion as well as growth of the refractories. The walls are often contained within steel frames, which are tied together with spring loaded tie bars. These are sized to provide the permissible maximum pressure on the specified refractories at operating temperature, which can be around 10 kg/cm^2 for magnesite bricks at 1100°C .

PLASMA ARC FURNACES

A plasma is a highly ionised high temperature gas and is generated by an open electric arc. The plasma is highly electrically conducting and can achieve current densities of 100 amps/cm^2 .

Plasma arc heating power can be produced by three methods:

1. DC arc, high current, low voltage (eg 10 kA, 125 V).
2. AC arc, high current, low voltage (eg 10 kA, 125 V).
3. DC plasma torch, low current, high voltage (eg 2.5 kA, 500V).

The arc may be struck between two electrodes or between an electrode and the melt. The latter case is termed a transferred arc.

With a DC free-burning arc (method 1), the attachment of the arc to the cathode covers a small area or spot, which tends to move around the surface of the cathode. Current densities at the attachment point are extremely high, some 100 times the average cathode current density. The expansion of the arc cross-section acts to draw surrounding gas into the arc and accelerate it toward the anode where it has a broad attachment. Because of the high temperatures at the cathode attachment, the only materials suitable for constructing cathodes are graphite or tungsten doped with thoria. Current densities are lower at the anode and the use of other materials is possible, such as water-cooled copper. In the case of AC arcs, the anode and cathode alternate and materials suitable for cathodes are required for both electrodes.

With the plasma torch, a flow of inert gas is supplied around the cathode to generate a well-defined flame of highly conductive gas. The current path may be from the torch containing the cathode to the melt, acting as an anode in which case it is a transferred arc, or may be between a cathode and anode within the torch giving a non-transferred arc. These arrangements are illustrated in Figure 17.2. The non-transferred plasma torch may be regarded as a gas heater.

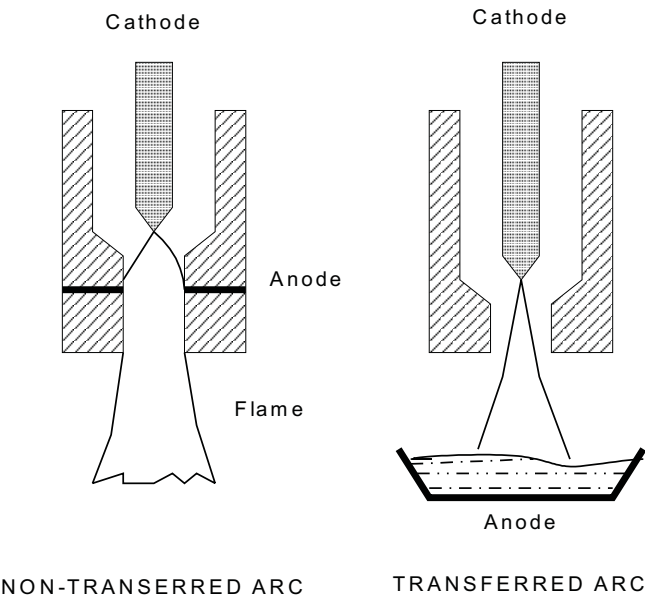


FIG 17.2 - Plasma torch arrangements.

- Heat is transferred from the arc to the furnace bath by three methods.
1. radiation from the arc,
 2. convection by gases circulated through the arc, and
 3. effects of arc attachment at the electrode itself.

The three mechanisms combine to deliver heat to the furnace bath and to the furnace itself. Part of the heat transferred to the furnace structure is re-radiated to the bath and the remainder is lost. The heat distribution to the bath is mainly by convection and is delivered most effectively by the DC arc. Table 17.2 lists the proportion of heat delivered to the bath by various means as a percentage of the supplied power. The remaining power is distributed to the furnace walls of which a proportion will be re-radiated to the melt.

The AC arc tends to fluctuate, is more unstable than the others, and generates more noise. The AC arc furnace is also characterised by deflections of the arc due to electromagnetic effects and a tendency to direct flames and splashes in a three lobe pattern to the walls of the furnace, damaging refractories. In

TABLE 17.2
Form of heat delivery to the molten bath.

Type of Arc	Radiation	Convection	Electrode Effect
DC Arc	10%	50%	12%
AC Arc	12%	45%	8%
DC Plasma Torch	10%	40%	3%

comparison, the DC arc provides a longer stable arc with more focused orientation. The longer arc allows for higher voltages and lower currents, reducing consumption of the graphite electrode. This effect is greatest with the plasma torch. The DC arc requires the electrode above the bath to be the cathode and the electrical connection to the bath to be positive. Bottom connections are made using steel blocks or steel pins fixed into a rammed refractory.

Due to their advantages, interest in the use of DC arc furnaces has increased with the development of efficient high power DC rectifiers.

The basic difference between the DC arc and DC plasma torch is that plasma gases are drawn into the arc from its surrounds in the case of the DC arc, but are supplied in the case of the plasma torch. Because of this, it is possible to inject powdered material into the plasma with the inert gas supply. This can be used to achieve rapid decomposition reactions, as well as fusion of highly refractory materials.

THE STERLING PROCESS

The original application of electric furnaces to commercial zinc production was the Sterling Process (Handwerk, Mahler and Fetteroff, 1952). This process used a rectangular reverberatory style brick lined water-jacketed furnace of the slag resistance type, fitted with three in-line electrodes. One furnace was operated by the New Jersey Zinc Company in Palmerton, New Jersey, two by the Cerro de Pasco corporation at Oroya, Peru, and one at the Belovo zinc smelter in Russia.

The furnace was charged with roasted zinc concentrates or oxidic materials, fluxes as required and sufficient carbon as coal for the reduction of the metals present, including part of the iron content. The charge mix was preheated in a rotary kiln fired with CO from the electric furnace. The preheating step removed moisture, coal volatiles and any carbonates present, and also resulted in the reduction of Fe_2O_3 to FeO. Flux additions were required to give a lime to silica ratio of between 0.8:1 and 1.4:1 so as to ensure a liquid slag at 1350°C.

The charge was banked around the periphery of the furnace, leaving an open area of slag around the electrodes. The electrodes could be held just above the surface of the slag or could be immersed, but the aim was to generate most heat at the surface of the slag from where it was transferred to the charge banks. Reduction reactions took place mainly in the solid charge and zinc was volatilised. The charge slowly melted to form the underlying slag layer and any metallic iron formed a pool on the base of the furnace below the slag. The formation of metallic iron needed to be minimised since it normally had little value and consumed energy and carbon. However, the level of iron in slag was controlled at less than six per cent, otherwise the metallic iron would be decarburised, raising its melting point and causing the formation of iron accretions. The level of iron in slag also needed to be above 1.5 per cent to avoid excessively reducing conditions and the reduction of silica, MgO and CaO. If there were excessive iron present in feed materials, sulfur could be added in the form of raw concentrates to form a matte rather than metallic iron. This also allowed for higher levels of iron in slag.

Zinc vapour and CO passed from the furnace to a zinc splash condenser for shock chilling of the gas and for zinc condensation. Gas leaving the condenser was scrubbed to recover residual zinc as 'blue powder' and the residual CO was used as fuel for feed pre-heating. Any lead present was also volatilised with zinc and was separated from condensed zinc by liquation. Iron was also separated as 'hard zinc' by liquation. Silver partly reported to zinc and to iron, but if a matte was formed it collected most of the silver as well as any copper and gold present.

The Sterling Furnace had a hearth of 4.88 m wide by 9.75 m long or 47.5 m². Maximum power rating was 6 MW (126 kW/m²) for a production 36 tonnes per day of slab zinc. Electrode energy consumption was about 2800 kWh per tonne of metals reduced. Zinc recovery from feed was around 95 per cent with full recycle of drosses and blue powder. The composition of any matte formed was typically 50 per cent Fe, 25 per cent S and ten per cent Zn, with copper and precious metals related to the feed.

THE SKF PLASMADUST PROCESS

The SKF Plasmadust Process was developed by SKF Steel in Sweden and a plant was constructed in Landskrona, in 1984 (Chalfant, 1996). The plant essentially uses a shaft furnace filled with coke and heated at the base by three Plasma torches, each with a power rating of 6 MW. Gas injected through the plasma torches is heated to between 2000 and 3000°C with an input of four to 5 kWh per Nm³ of gas.

Materials containing zinc oxide – primarily electric arc furnace (EAF) steel plant dusts – are injected through three tuyeres, each fitted with a plasma torch. The feed rate is around eight to 12 tonne per hour of EAF dusts containing 15 to 20 per cent zinc. Feed materials including coal and silica sand ground to minus 0.1 mm are prepared by mixing as a slurry in water to ensure complete homogenisation. They are then filtered and dried in a rotary kiln prior to injection through the tuyeres.

Reduction reactions take place mainly in or around the raceways that form in front of each tuyere. Zinc vapour rises with CO through the shaft and enters the condenser at a temperature of 1100°C. Molten iron and slag are tapped from the base of the shaft at a temperature of 1400°C. The amount of iron produced varies from 200 to 400 kg/tonne of EAF dust processed and is cast into pigs for use in the steel plant.

Gases leaving the condenser at 500°C are further cooled and scrubbed to recover and recirculate zinc collected as blue powder. Residual CO is partly compressed and recirculated to the plasma torches. The remainder of the gas is used for feed material drying. Typical consumption and production figures for this plant have been given as:

Electrical energy	1700 – 2000	kWh/tonne of EAF dust
Coal	0.1 – 0.2	tonne/tonne of EAF dust
Coke	0.05 – 0.15	tonne/tonne of EAF dust
Silica sand	0 – 0.08	tonne/tonne of EAF dust
Production	14 000	tonne/annum zinc
	19 000	tonne/annum iron
	30 000	tonne/annum slag

Initially three zinc splash condensers were installed but were subject to severe dross and accretion problems due to the presence of metallic iron and the formation of ‘hard zinc’ (Zn₁₃Fe). This condenser system was replaced with a lead spray condenser wherein lead is sprayed through nozzles into the hot gas stream. The lead is circulated through a cooling and liquation system along ISP principles to separate collected zinc and cool the lead for return to the condenser.

One unusual problem with this process was the formation of HCN in the high temperature highly reducing conditions. This reported to scrubber liquors giving a CN content of 1000 to 2000 mg/L and required treatment with hydrogen peroxide before waste water could be discharged.

For both technical and economic reasons, this process proved to be uneconomical for zinc recovery and was converted to the treatment of stainless steel dusts, having the capability of high temperature reduction required for chromium and ferroalloys. Any zinc and lead contained in furnace gases are now oxidised to form a fume and are collected by filtration for reduction to metal elsewhere.

OTHER ELECTRIC FURNACE PROCESSES

A number of electric furnace processes have been developed and operated for short periods of time to treat lead blast furnace slags, zinc leach residues and EAF dusts, with the production of zinc metal directly rather than zinc oxide. All have failed to materialise as long-term commercial operations, largely because of difficulties with accretions and dross formation within the condenser system. These attempts date back to a unit at the Herculaneum Lead Smelter in Missouri in 1942, to an operation at

Duisburg in Germany (Duisberger Kupferhütte) in 1961, and more recently to a number of attempts in the 1990s to process EAF steel plant dusts. The incentive to develop treatment processes arose from greatly increased environmental constraints imposed on the disposal of EAF dusts as landfill.

The ELKEM Multi Purpose Furnace

A multi purpose sealed electric furnace was developed by Elkem in Norway and applied for zinc recovery from EAF dusts at the Laclede Steel plant in Alton, Illinois (Pedersen, Aune and Cundall, 1990). The Elkem furnace is based on slag resistance heating, with a fully gas tight design and frozen slag lining based on cooling the furnace using a hot oil medium. The latter approach was intended to eliminate the need to compromise between optimum processing conditions and refractory life. The furnace is of circular construction with three graphite electrodes.

The process consisted of drying the feed, mixing with the carbon reductant and then briquetting with a water-free binder. Briquettes are screened to remove fines and are fed through a hopper system to the electric furnace. Since furnace gases have a high zinc content, a zinc splash condenser is used. Condenser gases are scrubbed and the collected solids are recycled. The scrubber liquors are treated with lime to precipitate zinc hydroxide, which is recycled to the feed.

Slag is continuously tapped from the furnace together with any metallic iron or lead formed. The formation of metallic iron is minimised since it is generally too impure to be marketable and is a significant consumer of carbon and energy. The primary objective was to produce an inert non-leachable slag suitable for landfill disposal.

The freeze lining approach allowed operation with a corrosive 'fayalite' (Fe_2SiO_4) slag without downtime for refractory replacement, and hence high availability. The compromise is an increased heat loss through the furnace walls of between 30 to 70 kW/m² compared with 20 kW/m² with refractory lined side walls.

It has been reported that zinc metal quality was poor and recovery of condensed zinc was little above 50 per cent, requiring a large recirculation of drosses and other materials. As a consequence, the Laclede Steel operation was not economical and was closed.

The TETRONICS Plasma Furnace

Tetronics Research and Development Company in the UK applied their DC plasma furnace to the treatment of EAF dusts (Cowx *et al*, 1990). The furnace uses a DC plasma arc transferred from a water-cooled cathode torch to the furnace bath, which is electrically connected by a steel billet anode built into the furnace hearth. The centrally mounted plasma torch is precessed to move the arc over a wide area of bath surface so as to distribute the energy, increase the bath agitation and improve the contact between the slag and the feed layer. Melt temperature is maintained around 1500°C. Mixed feed is blended with fluxes and reductant and is dropped through a port in the furnace roof. Furnace gases pass to an ISP zinc splash condenser and pig iron and slag are tapped intermittently. Dust carry-over was excessive and a hot coke gas filter was installed before the condenser but is understood to have been inadequate. Pelletising of feed was also evaluated.

A full scale plant was constructed in 1990 for Plazmet in Texas based on this approach but failed due to poor zinc recoveries to condensed metal and excessive drosses and accretions, which were difficult to recycle, particularly in relation to the halide content.

The AllMet Process

This process was also aimed at the treatment of EAF dusts and combined zinc fuming using a Direct Reduced Iron (DRI) rotary hearth furnace to fume zinc into a high grade oxide, with a Tetronics plasma furnace to reduce the oxide fume to metal. A commercial operation was constructed at the Nucor-Yamamoto Steel plant at Blytheville, Arkansas.

EAF and other steel plant dusts are mixed with coke fines and are pelletised. Green pellets are fed to an INMETCO rotary hearth furnace, which consists of a series of grates travelling on a circular track and supplied at various stages in this path with drying, heating and reducing gases to convert the pellets into high carbon iron or DRI. The hot DRI pellets are directly charged to an electric steel furnace or Basic Oxygen Furnace. Zinc and lead are fumed during the reduction cycle and are collected from furnace gases by bag filters after cooling. The collected dusts at around 70 per cent Zn content are then fed with coke fines to a Tetronics plasma furnace.

Major problems were still encountered with condenser drosses due to halides. Proposals to remedy this situation have included operating the zinc splash condenser at 650°C with a molten sodium and potassium chloride salt layer over the molten zinc bath in the condenser. This is intended to keep the dross fluid to avoid excessive build up of accretions and interference with the operation of the spray impeller. The higher temperature operation will in itself reduce the efficiency of the condenser by up to 2.5 per cent (see Chapter 11) (Pargeter, 1996). An alternative would be to leach halides from the collected fume prior to feeding to the plasma furnace. A second plant built at Jackson, Tennessee using these principles also had operating difficulties and was closed.

MINTEK Technology

The South African Mintek Research Group have developed and piloted a multi-purpose DC Plasma Arc furnace for general metallurgical applications including the treatment of EAF dusts, zinc leach residues and lead blast furnace slags (Barcza *et al*, 1995).

The circular furnace is lined with chrome-magnesite bricks and is fitted with one central graphite electrode (cathode). The anode connection is through the bath via a number of steel pins set into rammed refractory in the furnace hearth. The process also has the option of two furnaces in series. The first furnace would serve as a melting or holding furnace providing hot slag continuously to the second furnace where zinc reduction takes place. Coke is added to the reduction furnace, which operates at 1350°C.

Slag and pig iron are separately tapped from the reduction furnace and gases are sent to an ISP lead splash condenser. Metallic iron is produced with the processing of EAF dusts and lead blast furnace slags, and some lead bullion may be produced with the processing of zinc ferrite leach residues.

Zinc fuming rates in the range of 14 to 192 kg/h per m² of furnace hearth area are reported from pilot work when operating the reduction furnace at 1425°C with solid slag feeds, and 40 to 60 kg/h per m² when operating with molten furnace feed. These rates were critically influenced by coke reactivity, but fall well short of rates of over 200 kg/h per m² of hearth area for conventional slag fuming furnaces (Chapter 16). For EAF dust treatment, zinc fuming rates of 150 to 200 kg/h per m² have been obtained from dehalogenated fume. The Sterling Process achieved zinc fuming rates of 42 kg/h per m² of hearth area with dry feed.

This data indicates that reduction in the dry charge will be more efficient than from a relatively quiescent slag bath, and high turbulence and injection of carbon into the bath as in the conventional slag fuming furnace is highly beneficial to reaction kinetics. This situation is not present in an electric furnace.

In the process developed for treatment of EAF dusts, a dehalogenation step is included to reduce the chlorine content from 2.0 to 0.2 per cent and to reduce the severe impact on zinc condenser performance. The Mintek approach has yet to be commercially applied and considerable further development may be needed before all the problems associated with past process failures are overcome.

GENERAL CONCLUSIONS

This chapter has reviewed a long history of attempts to produce zinc metal directly by oxide reduction in an electric furnace. No process has yet succeeded in being commercially viable, however there are many valuable lessons and pointers to the prerequisites for successful direct reduction of zinc in an electric furnace.

Reduction and fuming rates for zinc are generally lower for electric furnaces in terms of hearth area than for other fuming methods. This may well be acceptable if metal is directly produced rather than a zinc oxide fume. However, there are major problems in all cases with the operation of the zinc condenser due to halides and dust carry-over, with low first pass recoveries to condensed metal. Many of these problems were apparent from early attempts at the process but were not recognised in the more recent spate of developments in the 1990s to treat EAF dusts.

It is apparent from these problems that the ISF shaft furnace provides a reasonable degree of filtration and removal of dusts prior to the zinc condenser and that this facility is absent from the electric furnace. The experience with the Plasmadust Process also suggests that even with the filtration facility, the presence of metallic iron in small amounts of dust or perhaps in vapour form is particularly detrimental to direct zinc condensation. The presence of halides is clearly also a major issue for zinc condensation and needs to be always be maintained below critical levels.

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Other Pyrometallurgical Reduction Processes

Apart from the major production processes using carbothermic reduction, there have been some attempts to develop novel approaches to zinc metal production. Two particular processes of interest are the Warner Process and the Outokumpu Iron Reduction Process.

THE WARNER PROCESS

In nearly all processes treating zinc sulfide concentrates, the energy released in oxidation of zinc sulfide and removal of sulfur is separated from the energy needs for the reduction of zinc to metal. The Warner Process attempts to integrate these separate steps into one, to recover available energy from zinc sulfide and the oxidation of sulfur, and to minimise the net energy input (Gray, 1993; and Fletcher and Gray, 2000).

The process was developed at the University of Birmingham in the UK by Professor Noel Warner to a small pilot scale, but remains to be commercially applied. A schematic of the essential elements of the process is shown in Figure 18.1.

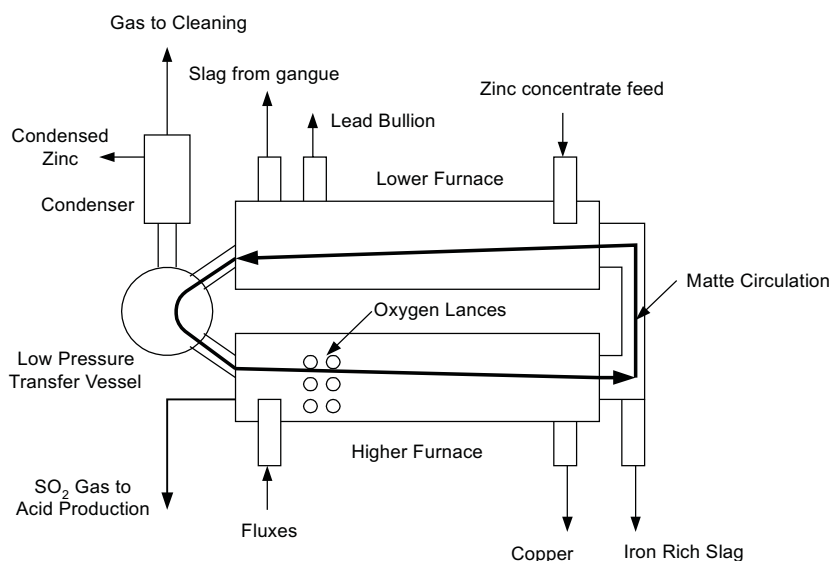


FIG 1 - Schematic of the Warner process.

The core of the smelter consists of two parallel rectangular reverberatory style furnaces with one about 30 cm higher than the other. A stream of hot molten copper rich matte circulates continuously through the two furnaces at 1150 to 1300°C. Zinc concentrates are added at one end of the lower furnace and are melted by the hot matte stream. Sulfides are dissolved reacting with the metallic copper contained in the matte in accordance with Equations 18.1 and 18.2.



Gangue minerals produce a slag which forms as an upper layer and overflows continuously through a tapping point at the opposite end of the furnace.

The matte stream is lifted from the furnace using the 'air lift' principle in which nitrogen gas is injected into a standpipe dipping into the matte and delivering it into an elevated vessel maintained at reduced pressure. Zinc vaporises into the gas stream and passes out of the collection vessel into a lead splash condenser. Some lead will transfer with the zinc to the condenser, but the bulk of the lead present will form a bullion layer on the bottom of the first furnace, which can be separately tapped.

Matte overflows from the collection or lifting vessel into the second higher furnace, and thus the lift vessel serves as a pump to circulate the matte stream. In the higher furnace, oxygen or oxygen-enriched air is injected through a series of non-splashing surface impingement lances. Sulfides are oxidised in accordance with Equations 18.3 and 18.4, and SO_2 is removed from the furnace.



An iron rich slag is formed from the FeO with the aid of added fluxes. The iron slag, as an upper layer, is tapped from the end of the furnace and the copper metal rich matte is re-circulated back to the lower furnace.

The slag formed from the melting of concentrates in the lower furnace represents the gangue components of the zinc concentrate feed and is of a relatively small volume. In the sulfide rich environment, it is also low in zinc content and normally represents a zinc loss of the order of one per cent. However, if there is any oxidised zinc present in the feed concentrates it will report to that slag and be lost.

The iron-rich slag produced in the oxidation furnace is of greater volume and is proportional to the iron content of the zinc concentrates. Since it is formed in contact with matte, it also has a low zinc content of less than three per cent. For a zinc concentrate containing 50 per cent Zn and ten per cent Fe, and for an iron slag at 40 per cent FeO, the loss of zinc in the iron slag will be around two per cent of zinc input. Allowing for some oxidised zinc present in the feed, losses from the furnace could be of the order of five per cent. In addition, the performance of the condenser will be critical. Losses in the form of condenser drosses and part of the blue powder formed will be in oxide form and will not be recoverable by recycling with the furnace feed.

There is a need to add small amounts of copper as copper sulfide concentrates to the feed to make up for losses in slags and lead bullion, which have been estimated at 2 to 3 kg per tonne of zinc recovered. However, if there is excess copper contained in the zinc concentrate feed then it is possible to tap a copper stream from the oxidation furnace. In that case, precious metals in the feed will be efficiently collected by the copper, otherwise they will report to the lead bullion stream.

Of the four principal reactions 18.1 and 18.2 are endothermic and 18.4 is strongly exothermic. It is possible to balance these heat requirements and make the process autogenous. To achieve this there must be sufficient iron sulfides present in the zinc concentrate feed, which may make thermal balancing of the furnace difficult in practice. However, this feature does mean that mixed low-grade concentrates can be readily treated by this process. It provides an opportunity for mine site application and for optimisation of metal recoveries from any given ore. Generally, if concentrates are shipped from a mine to distant smelters, the recovery of metals is compromised by the need to raise the grade of the concentrate to reduce tonnage related costs such as transport and smelter treatment charges, and so maximise economic returns. Since oxygen is used for matte oxidation, gases high in SO_2 content are produced and can be efficiently converted into sulfuric acid.

The zinc metal produced will contain a range of volatile impurities, possibly in greater amounts than for the ISF, which has a separate sintering stage to eliminate many highly volatile materials. The

deportment of such elements has yet to be fully defined, but it is likely that refining of condensed zinc will be required and that dross formation will be significantly higher than for the ISF.

The construction of the furnaces is based on similar furnaces used for copper smelting, and the matte transfer vessel is based on the RH de-gasser used in the steel industry. With the use of the lead splash condenser, the process has no unique equipment requirements. Unknowns that need to be evaluated by a full-scale plant relate to the deportment of minor elements and to the formation of accretion deposits and drosses or residues such as halide compounds, which may be difficult to handle and recycle, as well as creating significant potential problems with the condenser.

THE OUTOKUMPU IRON MELT REDUCTION PROCESS

Outokumpu Oy of Finland have proposed a process for the reduction of zinc oxides by direct injection with carbon as coke or coal fines, into molten iron with a carrier gas (European Patent, 1990; and Eerola, 1993). The iron melt serves as a medium for heat and mass transfer in the reduction reactions. Zinc oxides are reduced by the iron, and zinc metal is volatilised and removed with the carrier gas. The injected carbon dissolves readily in the iron and reduces any FeO to reform iron from the zinc reduction reaction to form CO. Because the dissolution of carbon lowers the melting point of the iron, the process can be carried out at temperatures at the lower end of the range of 1300 to 1500°C. Heat energy may be supplied either by indirect heating or by burning part of the carbon within the bath. Gases are processed in a zinc or lead splash condenser.

This process was never commercially developed, although it is understood that Outokumpu expended considerable development effort. In other processes, particularly as detailed in Chapter 13, practical difficulties are encountered with the presence of even small amounts of metallic iron in the zinc condenser due to the formation of 'hard zinc' accretions, even in circumstances where there is minimal metallic iron present in the reduction stage. Such problems are likely to be of a greater magnitude in this case.

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PART D

GENERAL AND COMPARATIVE ASPECTS OF MAJOR ZINC PRODUCTION PROCESSES

This part of the text covers the treatment of secondary materials and the comparative processing and economic aspects of the major extraction processes.

Chapter 19	Treatment of Oxide and Secondary Materials
Chapter 20	Energy Consumption
Chapter 21	Costs and economics of the Electrolytic Process
Chapter 22	Costs and economics of the ISF Process

Treatment of Oxide and Secondary Materials

SCOPE

Often oxides and secondary materials have unique problems in comparison with the treatment of standard concentrates. These problems usually relate to the presence of large amounts of one or more impurities. The following reviews major materials encountered under this category, the key issues involved in treatment and the methods normally applied. A range of both hydrometallurgical and pyrometallurgical methods can be used and reference is made to other relevant sections of the text where details of the various methods are given in more detail.

OXIDE ORES

Oxide ores of zinc are predominantly carbonates (Smithsonite/Calamine) or silicates (Willemite and Hemimorphite), or mixtures of both. Pure carbonates are commonly calcined for conversion to oxide prior to extraction of zinc. This may be carried out in a rotary kiln or a fluid bed calciner, and low temperatures of less than 500°C only are necessary for carbonate decomposition. Higher temperatures may be used if it is necessary to eliminate halides. The resulting oxide can then be leached in dilute sulfuric acid, such as spent electrolyte, to produce a zinc sulfate solution for subsequent electrolysis. Direct leaching of the carbonate is possible but generates CO₂ and can cause excessive foaming in the leaching tanks, which can be difficult to control.

Zinc silicates may be directly leached if the pH is below 2.5, to dissolve zinc and silica but form an unstable solution from which silica can readily precipitate as a gel. Conditions must be carefully selected to allow silica to precipitate in a controlled and crystalline form for separation by settling and filtration, and to enable the solids to be adequately washed free of entrained zinc. If a gel is formed, it is virtually impossible to filter and separate zinc from the precipitated silica (see also Chapter 5).

Different techniques have been developed for the direct leaching of silicate ores. The Padaeng Zinc plant in Thailand is one such commercial operation based on technology from Umicore in Belgium (Vieille Montagne process). Another is the Skorpion Project in Namibia, which uses direct leaching followed by solvent extraction of zinc.

Silicates can be leached under weak acid conditions at a pH of around two to give reasonably stable silica in solution (see Figure 5.2). By neutralising the resulting solution with ZnO or lime to a pH of around five at a temperature of 65°C or above, silica can be precipitated in a manageable form. The critical issue is to maintain the level of silica in solution in the neutralising-precipitation stage at low levels, and hence this stage should be operated continuously and preferably as a single stage rather than a series of reactors in series. The addition of seed in the form of recycled silica precipitate will also assist in the precipitation stage (Matthew and Elsner, 1977).

The Radino Process applied to Brazilian silicate ores used a batch leaching process in which aluminium sulfate is added with spent electrolyte to help coagulate colloidal silica and form a filterable solid (Radino, 1959). The influence of high valency ions such as Al³⁺ and Fe³⁺ in assisting silica coagulation or polymerisation is well known.

Silica is unstable in high acid conditions as well as at pH levels above four. Use can be made of this to leach silicates and simultaneously precipitate silica in a continuous leaching tank operating at an acidity above 2 g/L. As before, it is important to maintain the concentration of silica below a critical level to ensure that it does not form a gel and crystallises in a manageable form. This level is around 2 g/L. To ensure this, zinc silicate should be added to the leaching tank slowly, and a rate of addition equivalent to around 3 g/L of SiO₂ per hour has been specified (Fugelberg and Poijarvi, 1979). In this situation, preference must also be given to the use of a single stage continuous reactor.

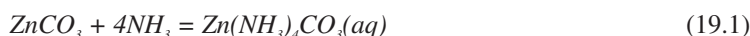
The Vieille-Montagne Process progressively leaches a zinc silicate ore in a series of continuous reactors at between 70 and 90°C by progressively increasing the acidity in each reactor. The total residence time is between eight and ten hours (Bodson, 1976).

Solutions derived from the direct leaching of carbonate and silicate ores need to be purified by standard methods as detailed in Chapter 6. However, additional prior iron purification may also be needed to remove impurities such as germanium and arsenic. This may require the addition of ferric iron to the leach solution before final neutralisation and precipitation of the iron. Precipitated silica can also be useful in removing some minor impurities such as germanium.

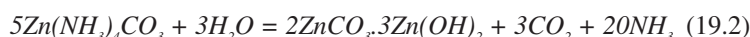
If the feed ores contain high levels of highly soluble impurities such as halides and magnesium then prior calcining would only remove the volatile halides but not magnesium. In that case, one option is direct leaching into a dilute solution followed by solvent extraction of the zinc from the leach solution and transfer into a higher concentration zinc sulfate solution for electrolysis. This has been applied at the Skorpion Zinc Project in Namibia (Garcia, Mejias, Martin and Diaz, 2000).

Pyrometallurgical processing (ie zinc fuming), may be applied to these ores to separate zinc as a high grade oxide for subsequent processing in an electrolytic plant or an ISF. The Waelz kiln has commonly been used for this purpose (see Chapter 16). Also, conventional slag fuming and the use of a submerged lance slag bath reactor are both applicable (Chapter 16). In general, the application of fuming methods adds significant costs and are probably only justified where difficult impurities are present or the grade of the ore is relatively low.

An interesting procedure first used for carbonate ores is the direct leaching with ammonia-ammonium carbonate solutions to dissolve zinc and form a zinc tetrammine complex in accordance with Equation 19.1.



After separation of leach residues, the solution is heated to boiling and the ammonia is stripped out with steam according to Equation 19.2. Zinc then precipitates as a basic zinc carbonate, which can be filtered from the remaining solution and calcined to a high grade zinc oxide as in Equation 19.3.



The process is highly selective for zinc and the zinc content of the resulting zinc oxide is around 79 per cent. This procedure can be used for extraction from carbonates or oxides but not from silicates. For oxide leaching, CO₂ needs to be supplied to the leaching stage. Ammonia from steam stripping is absorbed in water to reform the leach solution and is thus completely recycled. Only minor losses of ammonia need to be made up. However, balance controls for CO₂ are needed and for zinc carbonate treatment, lime neutralisation of reconstituted leach solution may be required to form CaCO₃ and to provide an outlet for CO₂, which will also be absorbed into the new leach solution from steam stripping vapours.

SECONDARY MATERIALS

Major secondary materials commonly constituting feed to smelting operations are galvanisers ashes and dross, and Electric Arc Furnace (EAF) dusts from the processing of steel scrap. Metallic scrap such as diecastings can also be a raw material source but are more commonly recycled either to reconstitute diecasting alloys or used as feed for zinc oxide production. In the latter case, zinc metal is heated in a crucible or furnace to produce a zinc rich vapour, which is burned in air to form zinc oxide. The oxide produced by this method has an ideal crystal structure for certain applications such as use as an additive in the manufacture of rubber.

Galvaniser's Ashes and Dross

Galvaniser's ashes are skimmings from the surface of a hot dip galvanising bath and are formed by oxidation of the zinc surface, which is accelerated by the dipping and withdrawal of work from the bath. A coating of zinc ammonium chloride flux can be used to reduce oxidation as well as assisting the galvanising process. The zinc content of ashes is usually between 65 and 75 per cent, partly as oxide and partly as metal and zinc chloride. Ashes are distinct from 'Galvaniser's Dross' which is a zinc-iron alloy taken from the bottom of the bath. It is commonly around 3.5 per cent Fe and 96 per cent Zn. Zinc is usually recovered from Galvaniser's Dross by distillation and is commonly the raw material for the manufacture of zinc oxide.

Ashes can be de-metallised by ball milling and screening to remove coarse metal prills. The fines can then be added directly to a roasting plant prior to feeding to the leaching section of an electrolytic plant. Roasting serves to eliminate the chloride content. Alternatively, it can be washed with a sodium carbonate solution to extract chloride while retaining zinc in the solids. Ashes can also be directly added to the feed of an ISF, but care must be taken to ensure that the chlorine load on the condenser is not excessive (see Chapter 14).

EAF Dust

EAF dust is formed during the melting of scrap steel in an electric arc furnace. It is composed of oxides of iron, zinc and other metals as well as volatile chlorides. It also contains fines from other components of the furnace charge such as lime, used to form slag. Typical composition of EAF dusts is given in Table 19.1.

Forty-five to 50 per cent of the zinc content is present as ZnO while the remainder is as zinc ferrite – ZnFe_2O_4 and some ZnCl_2 . Most of the iron is present as Fe_2O_3 .

Processing of EAF dusts attracted considerable attention during the 1990s and a number of processing options were developed. Most of these involved carbothermic reduction and direct condensation of zinc from reduction process gases. As detailed in Chapter 17, most of these processes failed due to heavy contamination of the condensation operation with dusts and halides. The major treatment method used for EAF dusts remains the Waelz Kiln fuming process (Chapter 16). Other fuming methods producing a zinc oxide fume, outlined in Chapter 16, are equally applicable and the zinc oxide fume is used as feed to an ISF or an electrolytic zinc plant (Assis, 1998).

The hydrometallurgical extraction efficiency of zinc from EAF dusts is relatively low due to the high proportion of zinc present as zinc ferrite, which is insoluble in a dilute acid leach or an alkali leach. Consequently, zinc extraction can be as low as 50 per cent and is not likely to be more than 70 per cent. To address this it is possible to recycle the leach residue to the electric furnace, but this requires the zinc extraction plant to be located close to the electric furnace rather than at a central location servicing a number of steel plants. In that situation the plant size is small and any economies of scale are lost. If the leach residue is recycled it should be mixed with pulverised coal and dried to less than ten per cent moisture. Otherwise, the ferrite residue can be leached in hot strong sulfuric acid, but iron must then be separated from the resulting solution in accordance with the methods discussed in Chapter 5.

A high level of halides is often present in EAF dusts, also presenting a problem for direct leaching and electrolysis using the standard sulfate electrolyte. One process developed to address this situation is the EZINEX Process developed by Engitec Impianti of Italy (Olper, 1998).

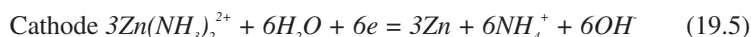
TABLE 19.1
Typical EAF dust composition.

Element	Range %
Zn	10 - 35
Pb	0.5 - 5
Fe	25 - 35
CaO	5 - 20
SiO ₂	3 - 5
Cl	1 - 5
F	0.5 - 1

Zinc oxide is leached from the EAF dusts with ammonium chloride solution in accordance with Equation 19.4 (see also Chapter 10).



The leach solution is purified by zinc dust cementation, and is then electrolysed depositing zinc metal on the cathode and oxidising ammonia at the anode instead of the formation of chlorine. The electrode reactions are as shown in Equations 19.5 and 19.6.



The avoidance of chlorine formation from a chloride electrolyte greatly simplifies the electrolytic cell, avoiding the need for diaphragms and a chlorine collection system, as well the disposal of chlorine or recycle to form HCl for leaching. However, this is at the expense of ammonia additions and about 0.18 tonne of ammonia is used per tonne of product zinc. At the Ferriere Nord Steel Plant in Udine Italy, where the EZINEX Process is installed, leach residues are recycled to the electric furnace and nominal capacity is around 2000 tonne per year of zinc metal.

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Energy Consumption

PURPOSE AND SCOPE

Energy use for the smelting and production of metals is an issue of some significance as the environmental consequences of energy production and use receive closer attention and scrutiny. Because energy consumption is a large cost factor in the smelting of base metals, this has also been an issue that has received close attention within the industry over many years. The purpose of this Chapter is to quantify, in a general way, the total energy use for the production of zinc by the major processes.

Whereas reduction processes use considerable quantities of carbon as coke, the electrolytic zinc process basically operates on electrical energy for metal reduction and for nearly all process equipment operation. It uses only small amounts of fuels such as oil and gas for some higher temperature process heating and the operation of mobile equipment. Since the electrolytic process is the predominant process in use, it is examined in greater detail herein as a benchmark for other processes.

ENERGY CONSUMPTION FOR THE ELECTROLYTIC PROCESS

The following provides generalised quantification of the various components of the energy balance for the electrolytic process and draws on generalised mass balance data for a plant using the jarosite process. The relevant components of that balance are as shown in Table 20.1 on the basis of one tonne of product zinc.

Concentrate Handling

The handling of incoming concentrates, their storage, blending and feeding to the roasting furnaces requires the use of mobile equipment and conveyor systems. Electric power used is around 5 kWh/t of concentrates handled or 10 kWh/t of product zinc. Fuels used for mobile equipment represents 150 MJ/t of product zinc.

Roasting (Assuming Fluid Bed Roasting)

The heat of combustion of zinc concentrates primarily reports to roaster gas and associated calcine leaving the roaster. Heat also reports to hot calcine discharged from the furnace and to cooling coils within the fluid bed, which in turn reports to steam. Heat in the gas offtake is partly recovered in the waste heat boiler and reports as steam. The heat of the combustion reaction is 4650 MJ/t of concentrate

Total steam production is generally of the order of 1.1 tonne per tonne of concentrate roasted and is at 40 bar and superheated to 400°C. The enthalpy of steam is 3090 MJ/t and the enthalpy of feed water is 440 MJ/t giving a net heat intake by steam of 2650 MJ/t. Hence the heat recovered in steam is 2915 MJ/t of concentrate roasted or 63 per cent of combustion heat. This equates to 5830 MJ/t of product zinc. Ten per cent of steam production can be used for deaeration of feed water and blow-down, leaving net output at 2.0 t/tonne of product zinc.

Electric power used for operating gas fans and conveyor systems, within the roasting plant, is typically 55 kWh/tonne of concentrate roasted, or 110 kWh/tonne of product zinc.

TABLE 20.1

Mass balance information (Jarosite Process).

Component	Quantity tonnes per tonne of product zinc
Concentrate roasted	2.0
Sulfuric acid produced	1.78
Lead / silver residue produced	0.1
Jarosite residue produced	0.53
Cadmium produced	0.003
Cathode zinc	1.075
Zinc dust	0.043
Zinc recycled in melting drosses	0.032

Fuel is used for roaster and acid plant start-up heating and for maintaining equipment temperatures during short term shutdowns. Although this fuel is used only for short periods, the average is taken as 400 MJ/tonne of product zinc.

Gas Cleaning and Sulfuric Acid Production

It is assumed that a conventional wet gas scrubbing system and double absorption acid plant are included. Power is used for fans and blowers as well as acid circulation pumps and cooling towers. Typical electric power consumption for plants based on nine to ten per cent SO_2 in roaster gas and six to seven per cent SO_2 in acid plant feed gas, is 120 kWh/tonne of acid produced. This equates to 214 kWh/tonne of product zinc. Fuel for preheating and start-up is included in the total roaster figure.

Leaching (Including Iron Removal)

Electric power is required for pumps, agitators, thickeners and filtration, and will vary considerably from one plant to another. Typical figures are of the order of 100 kWh/tonne of cathode zinc or 108 kWh/tonne of product zinc. Fuel is required for residue drying and is taken as 2000 MJ/tonne of lead-silver residue. This equates to 200 MJ/tonne of product zinc.

Spent electrolyte used for hot acid leaching of ferrite residues will need to be heated from around 40°C to close to 90°C for the leaching operation and additional heat input will be required for the precipitation of iron, taking the temperature closer to 100°C. On average, around 60 per cent of the total circuit solution flow follows this path. The estimated steam demand to heat the total solution flow is based on 0.0025 t of steam per m^3 of solution per degree C, and there is roughly 10 m^3 of solution associated with each tonne of cathode zinc. This allows for inefficiencies and heat losses in processing equipment and heats of reaction. Hence, for this demand, the quantity of steam required will be 0.9 tonne per tonne of cathode zinc, or 0.97 tonne per tonne of product zinc. This is used as saturated low pressure steam with a net available heat content of 2295 MJ/t and consequently represents a heat input to process of 2065 MJ/tonne of product zinc.

Solution Purification

As for leaching, electric power is required for pumps, agitators and filters and is estimated at 40 kWh/tonne of cathode zinc or 43 kWh/tonne of product zinc. Solution has to be heated to around 85°C for this operation requiring the use of additional steam. Effectively the remaining solution, which did not pass through hot acid leaching (40 per cent of the total), requires heating by approximately 45°C. As for leaching this is estimated at 0.45 tonne of steam per tonne of cathode zinc or 0.48 tonne per tonne of product zinc. This represents a heat input to process of 1102 MJ/tonne of product zinc.

Cadmium Plant

Cadmium is produced by leaching cadmium cementate, purification of the resulting solution, and electrodeposition of pure cadmium metal from the purified solution. The cadmium is melted and cast into ingots. Electric power required for the processing and electrolytic operations is taken as 2500 kWh/tonne of cadmium or 8 kWh/tonne of product zinc. Fuel is used for cathode melting and is taken as 700 MJ/t of cadmium or 2 MJ/tonne of product zinc.

Gypsum Removal

This section essentially consists of a series of large cooling towers for the circulation and cooling of purified solution and reduction of temperature to 25°C. Electric power is required for solution pumping and for cooling tower fans, and is taken as 30 kWh/t of product zinc.

Electrolysis

As indicated in Chapter 7 electrolytic power is typically 3026 kWhDC/t of cathode zinc at a current efficiency of 92 per cent and a cell voltage of 3.395. For a AC to DC conversion efficiency of 97.5 per cent this is 3104 kWhAC/t of cathode zinc or 3338 kWhAC/t of product zinc. In addition, there will be power for operating pumps, cranes, stripping machines, and cooling towers. This is taken as 60 kWh/t of cathode zinc or 65 kWh/t of product zinc.

Melting and Casting

It is assumed that all melting and holding furnaces are electric induction units as is the common practice. Requirements for melting are 105 kWh/t of cathode zinc or 113 kWh/t of product zinc. Power for holding furnaces and other operations such as ventilation systems, dross handling and milling, and zinc dust production will vary depending on the level of zinc alloy production but typically will be around 30 kWh/t of product zinc. Total power is then 143 kWh/t of product zinc.

Fuel is used in the form of natural gas or LPG for miscellaneous heating duties such as launders and mould heating and is taken as 80 MJ/t of product zinc. Fuel is also required for mobile equipment used for handling product ingot and is taken as 70 MJ/t of product zinc. The total fuel use is therefore 150 MJ/t of product zinc.

Effluent Treatment

Typical effluent treatment electrical energy requirements are taken as 20 kWh/t of product zinc. Steam may also be required if basic zinc sulfate treatment of electrolyte bleed solution is applied. A steam use of 0.1 tonne per tonne of product zinc is assumed or a heat input of 230 MJ/t of product zinc.

Residue Disposal

If jarosite residues are deposited in lined ponds, electric power is required for pumping residue slurries and return of any decanted solutions. The demand is taken as 10 kWh/t of jarosite residue produced or 5 kWh/t of product zinc.

Administration

Power demand to cover all offices and workshops, lighting and other general support functions is taken as 15 kWh/t of product zinc.

Surplus Steam Use

Steam production is 2.0 tonne per tonne of product zinc with an available heat content of 5830 MJ per tonne of product zinc.

Steam use as given above as LP steam is:

Leaching operations	2065 MJ/t of product zinc
Solution purification	1102
Other uses	230
Total use	3397 MJ/t of product zinc

Surplus steam heat available for power generation = 2433 MJ/t of product zinc.

If power is generated at 33 per cent thermal efficiency, then the equivalent of 803 MJ or 223 kWh can be generated per tonne of product zinc. For a 200 000 t/a zinc plant this would represent a generation capacity of 5.6 MW. Steam used for processing is generally low pressure saturated steam at around 4 bar. Hence the 40 bar steam generated by the roaster can be let down and desuperheated. Let down through a 'pass-out' turbine will generate electric power at relatively high thermal efficiency.

ELECTROLYTIC PLANT ENERGY USE SUMMARY

Energy use data for various sections of the process are summarised in Table 20.2. Steam demand has been expressed in terms of equivalent available heat transferred to the process. Electrical energy has also been expressed as equivalent fuel energy using a conversion factor of 1 kWh = 10.91 MJ, which assumes a thermal efficiency of 33 per cent for power generation.

TABLE 20.2

Summary of energy use per tonne of product zinc - electrolytic process.

Plant Section	Electrical Energy (KWh/t)	Electrical Fuel Equiv (MJ/t)	Fuels (MJ/t)	Steam (MJ/t)	Total Fuel Equiv (MJ/t)
Concentrate Handling	10	109	150		259
Roasting	110	1200	400		1600
Gas Cleaning/ Acid	214	2335			2335
Leaching	108	1178	200	2065	3443
Solution Purification	43	469		1102	1571
Cadmium plant	8	87	2		89
Gypsum Removal	30	327			327
Electrolysis- electrolytic	3338	36418			36418
- other	65	709			709
Melting and Casting	143	1560	150		1710
Effluent Treatment	20	218		230	448
Residue Disposal	5	55			55
Administration	15	164			164
Sub Total	4109	44829	902	3397	49128
Steam generated				-5830	-5830
Power Generation	-223	-2433		2433	0
TOTAL	3886	42396	902	0	43298

Table 20.2 indicates total fuel equivalent energy consumption of 49.1 GJ per tonne for zinc produced by the electrolytic process. This may be reduced by 5.83 GJ per tonne through the use of waste heat steam from roasting for process heating and for generation of power from the surplus. Of this total energy consumption, close to 74 per cent represents electrical energy required for electrolysis.

Heat released by the roasting reaction is 9280 MJ/tonne of product zinc, of which 5830 MJ/tonne is recovered as steam. Of this or 3397 MJ/tonne of product zinc is used for process heating and 2433 for power generation. This gives a net energy consumption of 45.7 MJ/tonne of product zinc without power generation and 43.3 MJ/t including by-product power generation. The waste heat recovered represents almost 12 per cent of total energy use, seven per cent is used for process heating and the remainder is available for power generation.

ENERGY USE FOR THE IMPERIAL SMELTING PROCESS

The first step in the ISF process is the sintering of feed concentrates and other feeds. This stage consumes fuel as gas or oil for ignition of the sinter charge. Sinter gases are relatively dilute in comparison with roasting and there is no opportunity to recover by-product steam. Energy consumption for gas cleaning and acid production is also marginally greater than for the roasting comparison due to the lower gas strength and relatively greater volume to be handled. The blast furnace uses approximately 1050 kg of coke per tonne of zinc produced, which is the major energy consumption. Low calorific value gas (LCV) from the process is used for preheating of the furnace blast air and for coke preheating.

For direct comparison with the electrolytic process it is necessary to include the refining of furnace zinc so that product zinc quality is similar. Natural gas or oil fuels are the major energy source for refining at around 6 GJ per tonne of product zinc.

The casting operations will source molten metal from the refining operation and hence energy use will be considerably lower than for the electrolytic process where cathode melting is required. In this case, it has been assumed that holding furnaces are heated by electric induction.

The ISF produces by-product lead bullion as well as zinc, and in order to strictly compare energy use for zinc production alone, it is necessary to take a credit for the energy otherwise required for the smelting of lead by the normal sinter plant-blast furnace route. This is taken as 11 GJ per tonne of lead bullion produced and excludes lead refining operations. If 0.4 tonne of lead bullion are produced per tonne of zinc, then the bullion energy credit is 4.4 GJ per tonne of zinc produced. Table 20.3 summarises the energy use for the ISF Process expressed in terms of total fuel equivalents as above, with 1 kWh of electrical energy equal to 10.91 MJ of fuel equivalent.

TABLE 20.3
Summary of energy use per tonne of zinc - ISF process.

Plant Section	Electrical Energy (kWh/t)	Electrical Fuel Equiv (MJ/t)	Coke (MJ/t)	Natural Gas (MJ/t)	Fuels (MJ/t)	Total Fuel Equiv (MJ/t)
Raw materials Handling	14	153			170	323
Sintering	180	1964		3200		5164
Gas cleaning/ acid	260	2837				2837
Blast Furnace	550	6000	29 925			35 925
Refinery	5	55		6000		6055
Casting plant	45	491		150		641
Plant services	20	218		5	20	243
Administration	10	109				109
TOTAL	1084	11 827	29 925	9355	190	51 297
Lead credit						-4400
NET TOTAL						46 897

Table 20.3 indicates that the total fuel equivalent energy consumption for zinc produced by the ISF Process is 46.9 GJ/t after allowing a credit for lead smelting. This is higher than the comparable figure for the electrolytic process if by-product steam is used to generate power, and very close if steam is not used for that purpose. However within normally expected variations the energy use for both processes is roughly the same.

If the electrolytic process uses hydroelectric power then it has a considerable energy advantage over the ISF, consuming 14.9 GJ per tonne of product zinc.

ENERGY USE FOR THE RETORT PROCESSES

Table 20.4 provides fuel and power consumption figures for the three major retort processes.

Energy parameters used for individual fuels are:

Coal	30.7 GJ/t
Coke	28.5 GJ/t
Electric power	3.6 MJ/kWh

In order to provide a direct comparison with the electrolytic process and the ISF process, it has been assumed that all subsidiary operations for a retort process are the same as for the ISF, simply replacing the blast furnace energy use given in Table 20.3 with a retort operation. All other process steps

TABLE 20.4*Power and fuel use for the retort processes.*

Process	Horizontal Retort	Vertical Retort	Electrothermic Retort
Power use (kWh/t)	140	250	2700
Coke for reduction (kg/t)	450	350	600
Coal for briquettes (kg/t)		830	
Coal for heating (kg/t)	1800	450	

including materials handling, sintering, gas cleaning and acid production, refining and services will all be the same in terms of unit energy consumption. Only the method of reduction of the sinter will be different. The result of this analysis is given in Table 20.5.

Retort processes consume much more energy than the ISF or electrolytic processes, with the old Horizontal Retort consuming about double the fuel equivalent. Since energy costs are a significant part of the total production cost it is clear why these processes have become obsolete.

TABLE 20.5*Summary of energy use per tonne of zinc for the retort processes.*

Process	Electrical Energy (kWh/t)	Electrical Fuel Equiv (MJ/t)	Coke (MJ/t)	Natural Gas (MJ/t)	Fuels/Coal (MJ/t)	Total Fuel Equiv (MJ/t)
Horizontal Retort Retort operation	140	1527	12 825		55 260	69 612
Other operations	534	5827		9355	190	15 372
TOTAL	674	7354	12 825	9355	55 450	84 984
Vertical Retort Retort operation	250	2728	9975		39 296	51 999
Other operations	534	5827		9355	190	15 372
TOTAL	784	8555	9975	9355	39 486	67 371
Electrothermic Retort Retort operation	2700	29457	17 100			46 557
Other operations	534	5827		9355	190	15 372
TOTAL	3234	35 284	17 100	9355	190	61 929

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Suggested Reading

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Costs and Economics of the Electrolytic Zinc Process

PURPOSE AND BASIS

The objective of this chapter is to provide a general outline of the costs associated with the Electrolytic Zinc Process as the predominant production process, and the factors affecting its economic performance. Because of inflation and other factors, which change cost structures, as well as differences in currency values from one country to another, it is difficult to provide cost figures that will remain meaningful with time. The primary purpose is therefore to provide a framework for cost analysis into which updated unit costs can be inserted, so as to develop updated cost estimates relating to a particular set of circumstances. The framework is aimed at identifying the major cost elements that need to be accounted for, as well as giving an indication of the relative importance of each cost component.

Information is drawn from personal sources within the industry and its suppliers, and from a range of published cost data. This data covers a long period of time and it has been necessary to update costs to the present time frame. All data has been expressed in US Dollars as at June 2000, and may be adjusted by CPI rates from that date.

CAPITAL COSTS

The construction costs for a new electrolytic zinc smelter have been developed for construction under USA or equivalent conditions. Construction costs in other localities will depend on the cost of construction labour, the use of local construction materials, and the extent of inclusion of locally manufactured equipment such as drives, filters, electrical supply equipment, etc. It needs to be recognised that for construction in lesser developed countries, the cost of individual labour may be substantially lower, but due to the lower labour productivity the overall labour cost component may not be greatly reduced.

Construction costs for remote locations can also be elevated due to the need to locate labour for the construction period. This may be minimised by off-site prefabrication of as much equipment as possible. Capital costs have been provided for typical 'green field' electrolytic zinc plants of 100 000 and 200 000 t/a zinc output. The assumed configuration of the sample plants is illustrated in Figure 21.1 and covers best current practice for a plant treating average sulfide concentrates by roasting and use of the jarosite process for iron separation. It is taken that jarosite residues are stockpiled in lined ponds.

In estimating the cost of different sizes of plant, the limiting size of individual units of equipment must be recognised, and duplication included if total requirements exceed that limit. An example would be the roaster where a limit of the order of 160 000 t/a of zinc production applies, representing the largest fluid bed roaster constructed to date. Similarly, the maximum size of electrolytic cell unit may be of the order of 220 000 t/a given the practical size of servicing equipment such as cranes and the limiting practical unit power supply voltage. These limits are by no means firm and tend to move with time, but they do tend to indicate levels within which there is a low risk of poor operating reliability.

Agitated tanks, thickeners and filters also have limits but other factors tend to determine the number used rather than a limiting size. These factors include the number of process stages required for reaction efficiency in a continuous process, the provision for equipment to be taken off-line for cleaning or maintenance without process disruption, or the number of filters required to allow integration of a batch operation into a continuous process. This level of detail has not been included in the general cost data provided. The subdivision of the plant cost areas is indicated in the diagram in Figure 21.1.

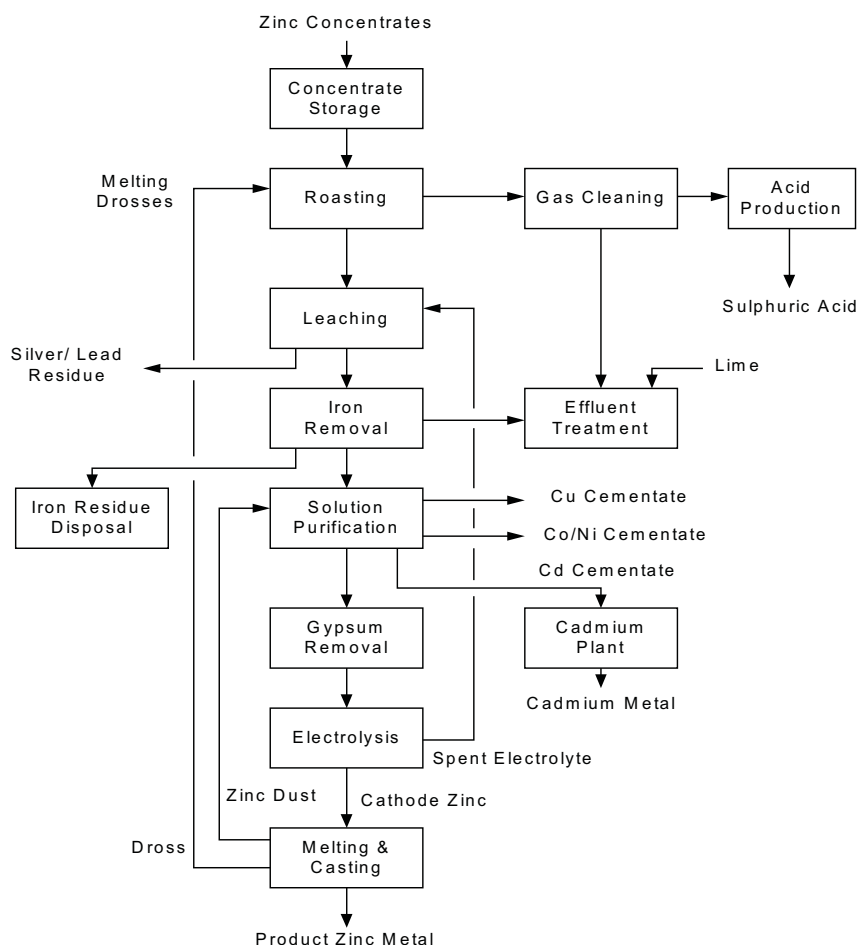


FIG 21.1 - Generalised flow sheet and plant subdivision.

The broad subdivision of costs as illustrated in Figure 21.1 may be defined as follows:

Concentrate Handling	Receival blending and storage facilities.
Roasting	Conventional fluid bed roasters of Lurgi design with one unit for the 100 000 t/a capacity plant and two units for the 200 000 t/a plant. Also includes calcine cooling and handling.
Acid Plant	Includes gas cleaning and a conventional double absorption acid plant based on a seven per cent SO ₂ feed gas.
Leaching	Includes Primary Neutral Leach, Hot Acid and Strong Acid leaching stages with separation of a lead-silver residue and separation of iron as jarosite.
Solution Purification	Includes three-stage zinc dust purification, separating a copper cementate, a cobalt/nickel cementate and cadmium.
Cadmium Production	Covers an electrolytic cadmium plant to treat cadmium cement and produce high-grade cadmium metal.
Gypsum Removal	Pure solution cooling facilities and separation of gypsum.

Electrolysis	Allows for one single cell unit in each plant size and includes solution cooling and storage, electrode handling and stripping facilities.
Melting and Casting	Covers one melting furnace for the 100 000 t/a plant and two melting furnaces for the 200 000 t/a plant, plus alloying furnaces slab casting and block casting equipment.
Effluent Treatment	Covers a lime neutralisation plant for processing weak acid effluent from gas cleaning, other process bleed streams and general effluents that cannot be recycled as process water.
Residue Disposal	Allows for rubber lined ponds to hold up to five years production of jarosite residue.
Utilities and Services	Allowance to cover the connection of power and water, drainage water collection works, maintenance facilities, laboratories and offices.
Site Works	Allowance to cover site earthworks, roads, access, fencing and drainage.

Costs given for each Section are fully constructed costs but exclude project engineering and supervision, which is estimated separately as 15 per cent of the project cost. Table 21.1 lists the capital costs for the two plant capacities under these conditions. Costs per annual tonne of zinc produced are close to \$2500 for 200 000 t/a and \$3000 for 100 000 t/a capacity.

For the marginal expansion of an existing smelter, many items can be reduced or eliminated by utilising existing services and utilities and it should be possible to achieve installation costs well under US\$2000 per tonne of zinc produced.

TABLE 21.1
Electrolytic zinc plant capital costs (June 2000).

Plant output t/a	100 000	100 000	200 000	200 000
Plant section	US\$ million	US\$/t of zinc	US\$ million	US\$/t of zinc
Concentrate handling	6	60	9	45
Roasting and calcine handling	27	270	50	250
Acid Plant incl Gas Cleaning	30	300	48	240
Leaching / Iron Separation	30	300	48	240
Purification	20	200	32	160
Cadmium production	4	40	7	35
Gypsum Removal	5	50	9	45
Electrolysis	58	580	94	470
Melting and Casting	18	180	30	150
Effluent Treatment	4	40	6	30
Residue Disposal	6	60	11	55
Sub Total	208	2080	344	1720
Utilities and Services at 12%	25	250	41	206
Site Works at 6%	12	125	21	103
Sub Total - Direct Plant Cost	245	2454	406	2030
Land and access	10	100	12	60
Licence Fees	5	50	7	35
Engineering at 15% of Direct Costs	37	368	61	304
Sub Total - Indirect Costs	52	518	80	399
Total Plant Capital Cost	297	2973	486	2429

Clearly circumstances and location will significantly change these figures, but Table 21.1 should provide a guide to the major items to be considered and the general order of cost for new facilities under USA conditions.

DIRECT OPERATING COSTS

Costs given in this section are for a modern highly automated plant as at June 2000.

Direct operating costs may be broadly subdivided into labour (for operating and maintenance), maintenance materials, electric power, and operating materials and supplies. Typical costs for a modern highly automated plant as at June 2000 are given in Table 21.2 for a plant of 100 000 t/a of annual capacity and in Table 21.3 for a plant of 200 000 t/a capacity. The subdivision of plant sections corresponds with capital cost items given in Table 21.1.

Labour costs are estimated from the number of employees required in each section covering both operating and maintenance, and an average annual employment cost of US\$50 000 per employee. Employment cost should be the total including direct wages and all associated expenses such as taxes, pension scheme costs, insurances, and benefits.

Power is estimated from typical consumption figures for each area and a power cost of four cents per kWh in this example. The major power consumption is for electrolysis and will not vary greatly from one plant to another, however consumption in other areas can vary considerably depending on process design and plant configuration.

Maintenance materials are simply estimated as two per cent of the direct construction cost for each Section. This cost will be lower for a new plant but should rise to the two per cent level for a well established plant. Materials and supplies are again typical in dollar terms and represent a range of reagents and consumables as well as external services provided to each section.

The cost of administration reflects higher salaried support and management staff, as well as services such as insurance and site taxes. These costs will vary widely depending on the location of the plant and whether it is a stand alone operation or part of an industrial complex.

As for the capital cost data, these figures are designed to provide a guide to the major operating cost items to be considered in any smelter evaluation. They are also reasonably typical with a total direct cost range from US\$380/t to US\$450/t of zinc produced for modern plants of 200 000 and 100 000 t/a output respectively.

TABLE 21.2

Direct operating costs for a 100 000 t/a zinc plant (costs in US\$ as at June 2000).

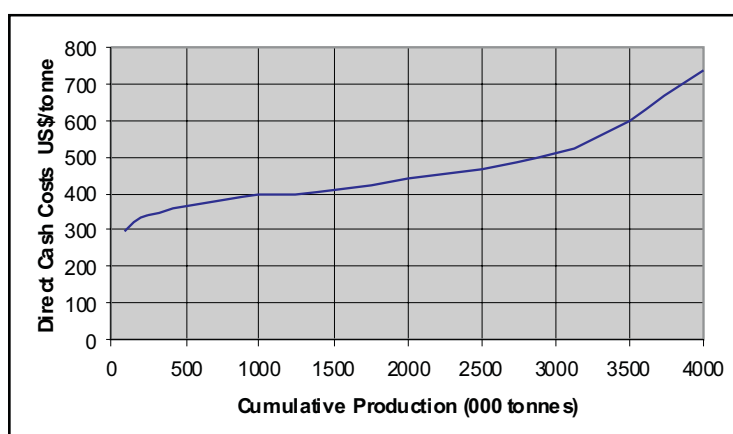
Plant Section	Number Employed	Power KWh/t	Labour Cost \$000s	Maint Materials \$000s	Electric Power \$000s	Materials and supplies \$000s	Total \$000s	Total \$/t
Concentrate handling	8	10	400	120	40	80	640	6.40
Roasting	35	110	1750	540	440	350	3080	30.80
Acid plant	25	200	1250	600	800	100	2750	27.50
Leaching/ iron sep'n	45	100	2250	600	400	750	4000	40.00
Purification	30	30	1500	400	120	275	2295	22.95
Cadmium production	12	15	600	80	60	60	800	8.00
Gypsum removal		30	0	100	120	10	230	2.30
Electrolysis	60	3300	3000	1160	13 200	1200	18 560	185.60
Melting & casting	50	150	2500	360	600	600	4060	40.60
Effluent treatment	10	20	500	80	80	180	840	8.40
Residue disposal	10	10	500	120	40	200	860	8.60
Administration	60	10	4500	125	40	2500	7165	71.65
Totals	345	3985	18750	4285	15 940	6305	45 280	452.80
Total per tonne of zinc			187.50	42.85	159.40	63.05	452.80	

TABLE 21.3*Direct operating costs for a 200 000 t/a zinc plant (costs in US\$ as at June 2000).*

Plant Section	Number Employed	Power KWh/t	Labour Cost \$000s	Maint Materials \$000s	Electric Power \$000s	Materials and supplies \$000s	Total \$000s	Total \$/t
Concentrate handling	10	8	500	180	64	150	894	4.47
Roasting	47	100	2350	1000	800	680	4830	24.15
Acid plant	33	180	1650	960	1440	200	4250	21.25
Leaching/ iron sep'n	50	100	2500	960	800	1480	5740	28.70
Purification	38	30	1900	640	240	550	3330	16.65
Cadmium production	16	15	800	140	120	110	1170	5.85
Gypsum removal		30	0	180	240	15	435	2.18
Electrolysis	90	3300	4500	1880	2640	2400	35 180	175.9
Melting and casting	90	150	4500	600	1200	1200	7500	37.50
Effluent treatment	12	20	600	120	160	330	1210	6.05
Residue disposal	12	8	600	220	64	400	1284	6.42
Administration	80	8	6000	206	64	4500	10 770	53.85
Totals	478	3949	25 900	7086	31 592	12 015	76 593	382.97
Total per tonne of zinc			129.50	35.43	157.96	60.08	382.97	

Competitive Cost Curve

The competitive position of a smelter in comparison with others is shown by use of the cumulative cost curve in which the direct cash cost for each of the world's smelters is plotted against the cumulative tonnage capacity, arranged in ascending cost order. The general form of the curve is shown in Figure 21.2 for Electrolytic Zinc Plants.

**FIG 21.2 - World Electrolytic Smelter Direct Cash Costs.**

This data shows that 85 per cent of production is from plants with direct operating costs within the range of \$340 to \$550 per tonne of zinc produced. The first quartile boundary is \$395 per tonne, and the third quartile upper boundary is \$510 per tonne. In terms of comparable cost curves the shape in this case for electrolytic zinc plants is relatively flat and has flattened over a significant period of time. This

corresponds with a mature commodity and mature technology, and indicates a highly competitive industry. The high cost end of the curve usually represents special situations for plants treating unique low cost feeds, such as secondary materials, and where it is possible to survive with high operating costs and often with small scale operations.

The above estimates indicate that the modern 200 000 t/a plant direct costs at \$383/t are just within the first quartile, whereas the 100 000 t/a plant costs at \$453 are close to the 50 per cent mark and are not particularly competitive, particularly considering the capital cost to be serviced. Many competing plants are fully depreciated and do not have capital servicing costs.

METAL PRICING

Generally zinc product prices are set by international metal exchanges, principally the London Metal Exchange (LME). Product price is therefore usually outside the control of the producer.

The demand for metals as commodities is determined by the international trade cycle. Supply and industrial demand are rarely in balance, and for this reason there is a need for an international terminal market as a gathering of traders to purchase and sell metal, provide a buffer stockpile and set prices according to net supply and demand requirements.

The LME has three functions in relation to metal trading:

1. To register prices as set by supply and demand trends. This is done on a daily basis.
2. To receive and deliver physical metal, which is held by traders in LME warehouses. A warrant is issued giving title to metal held in a number of warehouses worldwide.
3. To provide facilities for hedging contracts of which both forward selling and buying contracts are available.

The market trades seven base metals including zinc, and there are four opportunities to trade each day. Daily prices are quoted at the end of each morning trade as representative of the contracts made. Both a cash and three month forward delivery price are quoted. The three month price may be above the cash price (termed a 'Contango') or below the cash price (termed a 'Backwardation'). The LME market, in large part, reflects future expectations as well as current market conditions. Pricing is generally determined by market dynamics, considering factors such as:

- consumption demand and growth projections;
- supply chain projections for both mines and smelters; and
- stock holdings in smelters, LME warehouses, and with end consumers – or market liquidity.

The timing of changes in these market fundamentals can give rise to significant differences between the present and future metal prices. The involvement of option traders and hedge funds speculating on these balances is another important issue, and this activity can significantly influence pricing, deviating the market away from its underlying fundamentals in the short term. To some extent forward pricing is responsive to metal stocks, and will generally fall if stocks move well above normal levels, and vice versa.

The alternative to price setting by a terminal market is the use of a 'Producer Price', set by a cartel of producers, or by one major producer that others follow. This scheme was used up until the mid 1980s when both Producer Price and terminal market pricing schemes operated. Generally LME pricing is regarded as more independent, reflecting the market supply and demand balance. It can be manipulated by traders, but only over short periods of time. Metal can always be sold at negotiated prices between producer and consumer, but since the smelter is often separate from the mine supplying concentrate, a common metal pricing system is needed for both mine and smelter products, and the Producer Pricing approach is not particularly practical or equitable.

Metal held in LME warehouses must conform to set quality standards, and for zinc there are three standards as shown in Table 21.4.

TABLE 21.4
Standard zinc metal specifications.

Grade	Lead % Maximum	Cadmium % Maximum	Iron % Maximum	Zinc % Minimum (by difference)
Special High Grade	0.003	0.003	0.003	99.990
High Grade	0.07	0.03	0.02	99.90
Prime Western Grade	1.6	0.5	0.05	98.0

BY-PRODUCTS

For the typical Electrolytic Zinc Plant evaluated above, based on roast-leach-electrowin technology, the principal by-products will be sulfuric acid, copper cementate, and cadmium metal. Other possibilities, but generally with low returns, are gypsum, lead-silver residue and cobalt-nickel cementate, depending largely on the nature of the feed concentrates.

Sulfuric Acid

For a typical Roast-Leach operation sulfuric acid production will be close to 1.75 tonne per tonne of zinc produced. Of this, 0.2 tonne per tonne of zinc may be consumed within the plant if the jarosite process is used, leaving 1.55 tonne for sale. Internal consumption will be less for operations using the goethite process.

The net sale price for sulfuric acid will vary greatly depending on smelter location and proximity to acid markets, but by way of example is taken as US\$20 per tonne ex works. This represents a credit of $1.55 \times 20 = \$30.1$ per tonne of zinc produced.

In addition, the basic price of sulfuric acid as a traded commodity depends on the world market price of raw sulfur or brimstone. The supply-demand balance for brimstone can vary widely and is dependent on the general availability of smelter acid as well as other factors such as its production rate and the stock position. Given also that freight costs for shipping sulfuric acid from the smelter can be significant, particularly for smelters in remote locations, there are many situations where returns from acid sales can be negative, representing a disposal cost.

Regular output of acid is essential to maintain smelter operation, as storage is limited, and often there can be no option but to accept poor or negative returns.

Copper

Usually copper is produced as a cementate containing on average 0.012 tonne of copper per tonne of zinc produced. With a copper price of US\$1800 per tonne and payment for copper contained in the cementate at 75 per cent of the prevailing price, the credit is \$16.2 per tonne of zinc produced.

Cadmium

Cadmium production would typically average 0.3 per cent of zinc production or 0.003 tonne per tonne of zinc produced. At a value of US\$1.00 per pound, this represents a credit of \$6.60 per tonne of zinc produced.

Other By-Products

These are primarily lead-silver residue, gypsum and cobalt-nickel cementate. Often the returns from these materials are low and barely cover the cost of handling and transport to the customer. Credits are generally minor or may be negative and represent a disposal cost, and for the current example have been

ignored. This situation can change considerably depending on the particular concentrates being treated. In some instances other by-products such as germanium, indium, gallium and selenium can provide valuable returns to the smelter, but this is unusual.

SMELTER ECONOMICS

Smelter revenues are obtained from the sale of zinc metal and by-products. Generally zinc is sold at a premium to the LME price. The premium is in part established by the cost of accessing metal from alternative sources such as a LME warehouse or another supplier, and will vary according to the location of the customer. Premiums are also received for upgraded metal such as alloys and may range from continuous galvanising alloys with minor alloying component additions to specialised diecasting alloys. For the purposes of example, the overall metal price premium may be taken as an average level of US\$100 per tonne of zinc sold.

Costs borne by the smelter in producing zinc metal and alloys are:

- The cost of concentrates. In accordance with Chapter 3, concentrate feed has been costed on the basis of a 52 per cent zinc content, 97 per cent recovery of zinc to product metal and a Treatment Charge of US\$190 per tonne of concentrate at a zinc price of US\$1000 per tonne.
- The direct cash costs for the smelter operation. These have been detailed in Tables 21.2 and 21.3 for two different smelter capacities and for the roast-leach-electrowin technology.
- Annual capital expenditure required to sustain the smelter operation. This represents the ongoing annual expenditure on equipment replacement and modification. It may be estimated as 50 per cent of the cost of new plant spread over 30 years. This recognises an average plant life of 30 years and that part of the installation, such as structures, would not need replacement.
- The cost of delivery of product metal to the customer including handling, freight, insurance, and sales organisation expenses. This will vary greatly from one plant to another and will depend on relative locations of the smelter and its customers. These costs will be low for plants located in Europe and Japan, but will be high for plants located in Canada and Australia for example.

Zinc price is the main variable and uncertainty in any assessment of smelter economics, and is outside the control of the smelter operator. A new venture or investment in zinc extraction facilities, whether mine or smelter, must be able to withstand wide movements in the zinc price and at least remain cash positive at all points in the expected price cycle. Projection of future pricing is perhaps the most difficult issue and the greatest uncertainty facing any new investment.

For electrolytic zinc plants of 100 000 and 200 000 t/a capacity, and for a zinc price of US\$1000 per tonne, Table 21.5 provides a typical annual cost structure and economics based on the above data.

In this example, there is significant improvement in the economics of the larger scale operation. The 200 000 t/a operation achieves the major economies of scale, since at this point most major equipment items have reached maximum size. Thereafter duplication is needed and the benefits of scale are not as significant.

The returns on investment indicated would not normally be regarded as sufficiently attractive to justify investment and higher metal prices would be needed, or smelter costs substantially reduced. Particular costs requiring close attention are power and labour, which represent 30 per cent and 26 per cent of smelter related costs respectively for the 200 000 t/a plant. Otherwise, capital related costs (maintenance and sustaining capital expenses) representing 23 per cent of smelter related costs, should also receive attention.

The impact of zinc price on the margin, and return on investment, is given in Table 21.6. From this it can be seen that the margin increases by around \$40/t of zinc produced for every \$100/tonne increase in the zinc price. This reflects the distribution of zinc price gains between the concentrate supplier and the smelter and is a function of the concentrate purchase terms.

TABLE 21.5
Economics of electrolytic zinc plants.

Cost Item	100 000 t/a production US\$ per tonne of Zinc	200 000 t/a production US\$ per tonne of Zinc
Capital Costs	2973	2429
Revenues		
Zinc sales at LME price	1000	1000
Premium	100	100
Sulphuric acid	30.1	30.1
Copper cementate	16.2	16.2
Cadmium	6.6	6.6
Total revenue	1152.9	1152.9
Costs Raw materials	496	496
Direct operating	452.8	382.97
Sustaining capital	49.55	40.48
Delivery costs	50	50
Total costs	1048.35	969.45
Cash margin	104.55	183.45
As return on investment	3.52%	7.55%

TABLE 21.6
Effect of zinc price on smelter economics.

LME Zinc Price (US\$/t)	800	900	1000	1100	1200	1300	1400	1500
100 000 t/a Capacity								
Margin (US\$/t of zinc)	35	70	106	146	187	227	268	309
Return on Investment (%)	1.2	2.4	3.5	4.9	6.3	7.6	9.0	10.4
200 000 t/a Capacity								
Margin (US\$/t of zinc)	114	149	184	225	265	306	347	388
Return on Investment (%)	4.7	8.1	7.6	9.2	10.9	12.6	14.3	16.0

The general cost situation illustrated above indicates the relatively poor economics of zinc production as a mature commodity produced by a mature technology, and is the reason why so few new greenfield smelters have been constructed in the last two decades of the twentieth Century, particularly in the Western Economies where these economics prevail. Cost advantages are required to develop a viable operation, such as low labour or power costs, or lower cost raw materials. In terms of reduced raw materials costs the processing of secondary materials offers opportunities, but often the practical scale of such operations is quite small, offsetting the raw material cost advantage.

The major portion of capacity added in the last two decades of the 20th Century came from the expansion of pre-existing smelters ('Brownfields Expansion'), where considerably enhanced economics can be achieved.

It is of course not possible to generalise as in the above examples and a detailed assessment of each individual situation is necessary.

CAPACITY LIMITATIONS AND INCREMENTAL EXPANSION

As indicated above, Brownfields expansion provides the best opportunity to maximise economic returns from the production of zinc by the electrolytic process. However, some unit operations of the

process utilise large scale equipment and marginal expansion of these units in small increments will not be practical. This particularly applies to the roasting and acid production operations and to the cell house. Other areas such as leaching and solution purification can be expanded in an incremental way by the addition of extra tanks, thickeners and filters, as relatively small individual units.

Cell houses may have some flexibility, as they can be expanded by raising current density, but this may require marginal additional electric power supply and solution cooling. Stripping capacity can be accommodated to some extent by increasing deposition time, but all these measures will have a penalty in reducing electrical efficiency and raising power costs per unit of zinc produced. For marginal expansion, this can be justified up to certain limits, and then a new installation allowing reversion to optimum conditions can be made.

It is much more difficult to achieve capacity increments with roasting and acid plants. They are large units and are usually closely designed with little margin, particularly the acid plant. To a small extent, zinc throughput can be raised by purchasing higher grade concentrates with lower sulfur to zinc ratios, but at a significant cost penalty. Oxygen enrichment of fluidising air can also assist in raising roaster capacity but requires enhanced cooling of the roaster, and acid plant limits can quickly become a constraint.

To achieve significant marginal expansion without new large scale roasting-acid capacity, the use of zinc oxide as a supplementary feed is commonly used, the other option is the addition of direct concentrate leaching facilities. Direct leaching may entail high pressure leaching with oxygen or atmospheric pressure leaching as detailed in Chapter 5. Atmospheric pressure direct leaching can also be closely integrated with the use of the goethite process for control and removal of iron from solution.

Direct leaching of zinc concentrates as a supplement to a roast-leach plant has considerable simplicity since it can use calcine from the roasting step for neutralisation of the acidic solutions from a single stage direct leach. A ratio of 2:1 roast-leach to direct leach capacity would generally be close to the optimal upper limit of such a capacity addition.

Using combinations of the above measures can enable electrolytic zinc plants to be progressively expanded, without requiring large incremental additions to capacity, and can be the most economic approach to meeting increasing production demands.

Costs and Economics of the ISF Process

The following Chapter presents a brief generalised review of the costs associated with the ISF Process and the performance factors that affect its economics.

Information is drawn from personal sources within the industry and from generally published information updated to a reference date of June 2000. Cost structures between smelters will vary greatly depending particularly on the raw materials used and local costs for major items such as coke and labour. As for Chapter 21, it is aimed to provide a framework for identifying the major cost elements as well as indicating the relative importance of each cost component. All cost data is given in US dollars as at June 2000 and may be adjusted by CPI rates from the date.

CAPITAL COSTS

Since few ISF plants have been constructed after the 1970s, and since most existing plants have been progressively expanded and de-bottlenecked, data on original construction costs has very little relation to the present day construction cost of a new plant. However as a general guide, the installation of an ISF complex including sinter plant, acid plant, blast furnace, zinc refinery and casting plant, is more expensive than an electrolytic plant of comparable capacity by about ten per cent. For the 'standard' ISF of close to 85 000 t/a of product zinc output, the comparable electrolytic plant cost as indicated in Chapter 21 would be US\$3000 per annual tonne of zinc produced giving the cost of the ISF complex as US\$3300 per annual tonne of zinc produced, or US\$280 million for the standard plant. The broad flow sheet and subdivision of the plant is shown in Figure 22.1.

The subdivisions of the ISF plant may be defined as follows:

Concentrate Handling	Receipt and storage of raw materials, controlled blending of feeds and flux materials to constitute sinter plant feed.
Sinter Plant	Conventional updraught sinter plant including feed mixing with return sinter, feed conditioning and moisture control, sinter strand, product sinter crushing and screening, sinter storage.
Acid Plant	Includes gas cleaning and a conventional double absorption acid plant based on gas around six per cent SO_2 strength.
Blast Furnace	Covers Coke supply and pre-heater, furnace charging system, blast air supply and preheaters, shaft furnace, zinc condenser and molten zinc separation, slag tapping and granulation, lead bullion tapping and copper drossing facilities.
Zinc Refinery	Holding furnaces and remelt facilities, operating and stand-by distillation columns.
Casting Plant	Molten zinc holding furnaces, slab and block casting facilities.
Cadmium Plant	Covers sinter plant fume leaching and cementation equipment, feed melting and holding furnace, distillation column and cadmium metal casting facilities.
Effluent Treatment	Covers a lime neutralisation plant for processing weak acid effluent from sinter gas cleaning and other liquid waste streams.
Slag Disposal	Includes facilities for the handling and disposal of granulated slag. This may simply be site stockpiles.

Utilities and Services	Allowance to cover the connection of power and water, drainage water collection works, maintenance facilities, laboratories and offices.
Site Works	Covers site earthworks, roads, access, fencing and drainage.

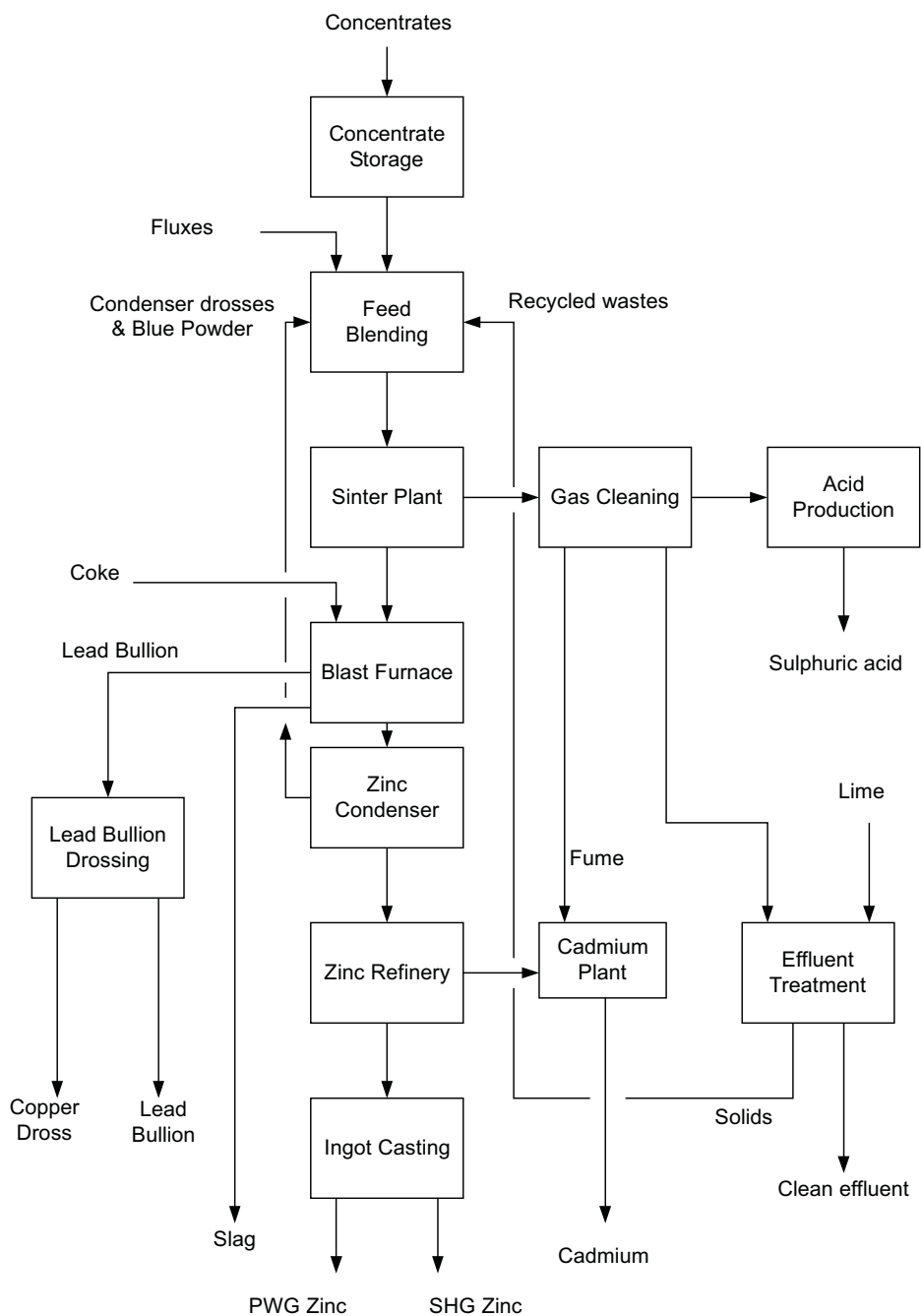


FIG 22.1 - Generalised flow sheet and subdivision of the ISF.

DIRECT OPERATING COSTS

Costs are given in this section for the Standard ISF Plant as at June 2000. Direct operating costs have been broadly subdivided into labour (for operating and maintenance), maintenance materials, electric power, coke, and other operating materials and supplies. Typical figures for the standard plant producing 85 000 tonne per year of product zinc metal are given in Table 22.1.

TABLE 22.1

Indicative direct operating costs for a standard ISF (costs in US\$ as at June 2000).

Plant Section	Labour Nos	Labour Cost \$000s	Maint Materials \$000s	Power Cost \$000s	Coke/Fuels \$000s	Materials and Supplies \$000s	Total \$000s
Feed handling	12	600	100	60		75	835
Sinter Plant	45	2250	2020	765	816	850	6701
Acid Plant	20	1000	600	1105		280	2985
Blast Furnace	90	4500	3500	1488	11 600	2800	23 888
Refinery	45	2250	650	22	1530	2500	6952
Casting Plant	45	2250	250	191	40	500	3231
Effluent Treat	10	500	40	50		100	690
Slag disposal	10	500	40	35		400	975
Administration	55	4125	100	43	10	2200	6478
Total	332	17 975	7300	3759	13 996	9705	52 735
Total per tonne		211	86	44	165	114	620

Labour costs are based on the number of employees required for each section covering both operating and maintenance, and an average annual employment cost of US\$50 000 per employee. Employment cost should be the total including direct wages and all associated expenses such as taxes, pension scheme costs, insurances and benefits.

Power is likely to be higher cost than for a comparable electrolytic plant due to the much lower use, and has been estimated on the basis of six cents per kWh and in comparison with 4 cents per kWh for the electrolytic plant. Coke costs are likely to be quite variable depending on plant location and access to coke supplies, but are taken as US\$130 per tonne for this exercise. This equates to approximately US\$4.6 per GJ. Other fuels may be oil or natural gas for sinter plant ignition and for operation of the refining columns. Costs for natural gas at US\$3 per GJ are used in this case.

Maintenance materials are typically 2.5 per cent of direct construction costs for new plant. Materials and supplies are also typical figures and represent all necessary fluxing materials, reagents and consumable supplies as well as external operating services.

The cost of administration covers salaried support and management staff, as well as administrative services, insurances and site taxes. These costs will vary widely depending on the location of the plant and whether it is a stand alone operation or part of an industrial complex.

The costs given in Table 22.1 are typical given the unit costs used and indicate a direct production cost of US\$620 per tonne of product zinc. This is substantially higher than the typical range for the electrolytic plant as given in Chapter 21 at between US\$380 and US\$450 per tonne depending on plant size. However, the ISF costs has higher by-product credits for lead bullion in particular, and is able to access bulk concentrate feeds at lower unit cost. This is offset to some extent by the lower returns from product zinc metal with a significant proportion being Prime Western Grade.

PRODUCT ZINC PRICING

In line with the economics for the Electrolytic Zinc process given in Chapter 21, zinc metal is priced by the London Metal Exchange with a basic LME quotation for Special High Grade specification of US\$1000 per tonne. Prime Western Grade is discounted below the SHG price and for illustrative purposes the discount has been taken as US\$50 per tonne. This discount will vary substantially depending on the supply and demand balance for this grade of metal at any particular time.

As indicated in Chapter 21, product metal can also receive a supply premium above the LME price depending on location of the customer and the cost of accessing the metal from a LME warehouse or other sources. In the previous example, a premium of US\$100 for SHG zinc was assumed for economic evaluation purposes. If the same supply premium applies to both grades, then the return on product metal from the ISF (at a LME price of US\$1000 per tonne) would be US\$1100 per tonne for the SHG product and US\$1050 for PWG product zinc. In reality, the supply premiums will not necessarily be the same for different product grades.

These returns must be offset by the cost of delivery of product metal to the customer, including handling, freight, insurance, and sales organisation expenses. These costs will vary greatly depending on the location of the smelter and its customers. For comparative purposes, these costs are taken as US\$50 per tonne of product zinc.

BY-PRODUCTS

The principal by-products from an ISF are lead bullion containing silver and gold, copper dross, sulfuric acid and cadmium. Amounts and composition of by-products will critically depend on the composition of the feed materials. For the purposes of illustration, the following typical mass balance has been used:

Bulk concentrate feed	230 000 tonne per year 40% Zn 20% Pb 150 g/t Ag 1% Cu 30% S
Product zinc	25 000 tonne of Special High Grade quality 60 000 tonne of Prime Western Grade quality containing around 1000 tonne of lead
Lead bullion	43 000 tonne per year 42 000 tonne Pb 450 tonne Cu 29 000 kg of Ag
Copper dross	4200 tonne per year 2100 tonne of Cu (50%) 1460 tonne of Pb (35%)
Cadmium	340 tonne per year
Sulfuric acid	190 000 tonne per year
Slag	72 000 tonne per year

Lead Bullion

Lead is derived from concentrates processed as well as from refined lead make-up added to the condenser, which represents around two per cent of product zinc. Some condenser lead is lost in product zinc and in condenser drosses and 'Blue Powder'. The latter materials are recycled and the contained lead reports to Blast Furnace bullion. Total lead bullion production is usually in the range of 40 to 50 per cent of zinc metal production. The content of precious metals will vary widely depending on the concentrates used, but for an average feed of 40 per cent Zn, 20 per cent Pb and 150 g/t Ag, the bullion contains 675 grams of silver per tonne.

At a lead price of US\$600 per tonne and a silver price of US\$5 per troy ounce, the value of bullion under normal commercial terms paid by a lead refinery is close to US\$570 per tonne of bullion, which represents close to US\$285 per tonne of product zinc.

Copper Dross

The majority of copper entering the system reports to the lead bullion and is separated as a surface dross when the bullion is cooled prior to casting into block ingots. Sulfur can be added to assist in copper removal into dross, but generally copper levels in bullion are reduced to below 0.1 per cent. The copper dross normally contains around 50 per cent copper and 35 per cent lead and is sold to copper smelters. Purchase terms return about 75 per cent of the contained copper value and, for a copper price of US\$1500 per tonne, the above balance would indicate a by-product credit of US\$27 per tonne of zinc produced.

Cadmium

Cadmium production varies widely depending on feed materials, but typically averages around 0.4 per cent of zinc production. At a value of US\$1 per pound this represents a credit of US\$8.8 per tonne of product zinc.

Sulfuric Acid

Sulfuric acid produced from sinter gas is 'black' in colour rather than 'clear' or 'white' as derived from roasting operations. This is due to the presence of organic compounds such as flotation reagents in sinter plant gases, which distil from the sinter feed as it is heated ahead of the combustion of sulfides. The organic compounds are absorbed from the gas stream into drying tower acid and are decomposed by the strong acid to form finely divided carbon, discolouring the product acid. Because of this, the acid has limited application – such as use in the manufacture of fertilisers, otherwise it must be treated to remove the coloration by oxidation with hydrogen peroxide. In either case, the net return from sale of 'black' acid is at a discount to 'white' acid. The discount will depend on the proximity of suitable customers, but for example, may be taken as around US\$10 per tonne. In comparison with the sale of 'white' acid at US\$20 per tonne, the net return in this case will be around US\$10 per tonne.

With the production of 2.5 tonne of acid per tonne of product zinc from low grade concentrate feeds, the credit is US\$25 per tonne of zinc produced.

SMELTER ECONOMICS

The basic parameters used in this example are similar to those applied in Chapter 21 for evaluation of the economics of the electrolytic zinc process, so that the two processes can be compared. The most significant cost item is the cost of feed, which can vary significantly depending on the grade of the concentrate used and indeed the degree of use of residues and other secondary materials. The basic mass balance data given above is based on the use of bulk concentrates containing both zinc and lead. It is

also possible to use a mix of high grade zinc and high grade lead concentrates, but at premium cost. To some extent, the use of high grade concentrates will enable production to be increased. This is due to the reduced sulfur content of the concentrates per tonne of metal produced, allowing increased tonnages of metal to be handled by the sinter plant for the same sulfur burning load. Control of the sinter plant is also likely to be easier with improved average sinter quality, thus improving blast furnace performance. Slag quantities will also be reduced enabling increased blast furnace capacity for the same coke consumption rate. The actual increase in production possible will depend on where the main plant restriction lies. It can be maximised if the main restriction is in the sinter plant.

TABLE 22.2
Economics of the standard ISF smelter.

Item	Bulk Cons Feed	High Grade Cons Feed	High Grade Cons Feed
Zinc Production t/a	85 000	85 000	95 000
Bullion production t/a	42 400	42 200	47 200
Sulfuric acid production t/a	216 000	185 000	207 000
Slag production t/a	84 300	76 800	85 900
Zinc recovery to metal %	93.0%	93.6%	93.6%
Revenues (US\$ per tonne of product zinc)			
Zinc metal revenue	1065	1065	1065
Bullion revenue	284	280	280
Sulfuric acid revenue	25	22	22
Copper dross revenue	27	27	27
Cadmium revenue	9	9	9
Total Revenue	1410	1403	1403
Annual Costs (US\$ per tonne of product zinc)			
Concentrate costs	532	699	699
Direct operating costs	620	620	584
Delivery and realisation costs	77	77	77
Total costs	1229	1386	1360
Cash Margin (US\$ per tonne of product zinc)	181	17	43

Table 22.2 indicates the comparative economics of a standard ISF with a nominal zinc output of 85 000 tonne per year based on a bulk concentrate feed. It also illustrates the economic performance with use of high-grade concentrates for both the same zinc production and for increased zinc production to the maximum extent based on a sinter plant limitation.

Table 22.2 indicates a substantial decrease in cash margin if high-grade zinc and lead concentrates are used as feed. The ability to raise production of zinc by using high grade concentrates assists by raising the cash margin, but is insufficient to offset the penalty of using higher cost concentrates in place of bulk mixed concentrate. This illustrates the key issue for ISF smelters: that viable operation depends critically on the sourcing of low cost feed materials. The use of residues and secondary materials to the maximum possible extent can also enhance margins further and offset marginal reductions in zinc production that may occur. It should be noted that there are limits to the quantity of inert residues that can be added to a sinter plant feed due to heat balance and sinter quality considerations. Sinter quality can deteriorate as the proportion of residues or inert materials increases, which in turn can affect blast furnace performance and reduce production.

Inert oxide feeds can be added directly to the blast furnace in the form of briquettes to supplement sinter, and this is an effective way of increasing production from low cost residue feeds.

In comparing the standard ISF smelter data in Table 22.2 with the electrolytic smelter of comparable capacity at 100 000 t/a of zinc output, the cash margin for treatment of high grade concentrate feed is US\$104 per tonne of zinc (see Table 21.5). This rises to US\$183 per tonne for a plant of 200 000 t/a capacity. For comparable high-grade concentrate feeds, the ISF does not compete with the electrolytic zinc plant. The ISF is only competitive if it operates on bulk and low cost concentrate feeds.

The ISF clearly only has a place for the treatment of low grade mixed zinc and lead concentrates, which cannot be handled by the electrolytic plant, and for the treatment of secondary materials. Viability depends on accessing relatively low cost feeds.

Properties of Zinc and Associated Compounds

ZINC METAL PROPERTIES

Atomic number	30							
Atomic weight	65.37							
Stable isotopes, relative abundance								
Mass number	64	66	67	68	70			
Per cent abundance	48.89	27.81	4.07	18.61	0.62			
Melting point	419.4°C							
Boiling point (at 760 mmHg)	907°C							
Density: Solid at 25°C	7.14							
Solid at 419.5°C	6.83							
Liquid at 419.5°C	6.62							
Liquid at 907°C	6.24							
Coefficient of linear thermal expansion (polycrystalline)	39.7 x 10 ⁻⁶	°C ⁻¹						
Coefficient of volumetric thermal expansion	89.3 x 10 ⁻⁶	°C ⁻¹						
Heat capacity of solid	22.4 + 0.01005 . T	J.mole ⁻¹ .°C ⁻¹ (T in °K)						
Heat capacity of liquid	31.4	J.mole ⁻¹ . °C ⁻¹						
Heat capacity of vapour	20.786	J.mole ⁻¹ . °C ⁻¹						
Heat of fusion	7384.76	J.mole ⁻¹ at 419.4°C						
Heat of vapourisation	114767.12	J.mole ⁻¹ at 907°C						
Thermal conductivity of solid (25°C)	1.13	J.sec ⁻¹ .cm ⁻¹ .°C ⁻¹						
Thermal conductivity of solid (419.4°C)	0.96	J.sec ⁻¹ .cm ⁻¹ .°C ⁻¹						
Thermal conductivity of liquid (419.5°C)	0.61	J.sec ⁻¹ .cm ⁻¹ .°C ⁻¹						
Thermal conductivity of liquid (750°C)	0.57	J.sec ⁻¹ .cm ⁻¹ .°C ⁻¹						
Liquid surface tension	7.58 – 0.0009.(T – 419.5°C)	Nm.cm ⁻¹						
Electrical resistivity at 20°C (polycrystalline solid)	5.46.(1 + 0.0042.T).	10 ⁻⁶ ohm.cm ⁻³						
Electrical resistivity at 423°C (liquid)	36.995 . 10 ⁻⁶	ohm.cm ⁻³						

CADMIUM METAL PROPERTIES

Atomic number	48							
Atomic weight	112.40							
Stable isotopes, relative abundance:								
Mass no	106	108	110	111	112	113	114	116
Per cent	1.22	0.88	12.39	12.75	24.07	12.26	28.86	7.58

Melting point	320.9°C	
Boiling point (at 760 mm Hg)	765°C	
Density (Solid at 25°C)	8.642	
Coefficient of linear expansion (solid)	$20 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$	
Heat capacity of solid	$22.22 + 0.0123.T$	$\text{J.mole}^{-1}\text{ }^{\circ}\text{C}^{-1}$ (T in $^{\circ}\text{K}$)
Heat capacity of liquid	29.71	$\text{J.mole}^{-1}\text{ }^{\circ}\text{C}^{-1}$ (T in $^{\circ}\text{K}$)
Heat capacity of vapour	20.8	$\text{J.mole}^{-1}\text{ }^{\circ}\text{C}^{-1}$ (T in $^{\circ}\text{K}$)
Heat of fusion	6108.6	J.mole^{-1} (at 320.9°C)
Heat of vapourisation	99 872.1	J.mole^{-1} (at 765°C)

THERMODYNAMIC PROPERTIES OF COMPOUNDS INVOLVED IN ZINC EXTRACTION

(Source: Handbook of Chemistry and Physics – CRC).

Compound	Mol Wt	Density (298°K) g/cm ³	Heat of Formation (298°K) kJ/mole	Free Energy of Formation (298°K) kJ/mole
ZnS -sphalerite	97.44	4.102	-202.92	-198.32
ZnS - wurtzite	97.44	4.087	-189.53	-184.93
ZnO	81.38	5.606	-348.38	-318.19
ZnSO ₄	161.45	3.74	-978.55	-871.56
ZnSO ₄ .7H ₂ O	287.45	1.966	-3075.66	-2560.19
ZnCO ₃	125.39	4.42	-812.53	-731.36
Zn ₂ SiO ₄	222.85	4.05		
ZnCl ₂	136.29	2.91	-415.89	-369.27
Zn (g)	65.37	0.0029	130.44	94.93
FeS ₂	119.98	5.0	-177.90	-166.69
FeS	87.91	4.6	-95.06	-97.57
FeO	71.85	5.7	-266.52	-244.35
Fe ₂ O ₃	159.69	5.24	-822.16	-740.99
SiO ₂	60.07	2.65	-859.39	-805.00
SO ₂	64.06		-296.81	-299.91
H ₂ SO ₄	98.06	1.834	-810.40	-733.92
CaCO ₃	100.09	2.711	-1211.13	-1133.03
CaO	56.08	3.32	-634.71	-603.75
CaSO ₄ .2H ₂ O	172.14	2.32	-2005.52	-1780.17
PbS	239.27	7.5	-94.31	-92.67
PbO	223.21	9.53	-217.86	-188.49
PbSO ₄	303.27	6.2	-918.39	-811.24
CO (g)	28.01	0.00125	-110.54	-137.28
CO ₂ (g)	44.01	0.00197	-393.51	-394.38
CH ₄ (g)	16.04	0.000717	-74.85	-50.79
H ₂ O (g)	18.01		-241.84	-228.59

HEAT CAPACITIES AT CONSTANT PRESSURE

(Joule. mole⁻¹. °K⁻¹ as a function of temperature T°K):

$$C_p = a + b T + c T^2 + d T^{-2}$$

suitable for elevated temperatures around 1000°C.

Compound	a	b	c	d
Zn (g)	20.786			
ZnO	49.003	0.005104		-912 279
ZnS	49.246	0.005272		-485 344
ZnSO ₄	117.152			
ZnCl ₂	66.526	0.03347		
FeS ₂	74.768	0.005565		-1 274 028
FeS	50.417	0.01142		
FeO	52.802	0.006242		-318 821
Fe ₂ O ₃	103.428	0.06711		-1 771 506
Fe ₃ O ₄	172.255	0.07874		-4 098 228
Fe (solid)	25.606	0.01406		
Fe (liquid)	34.10			
PbS	44.476	0.01678		
PbO	43.221	0.01331		
PbSO ₄	110.458			
Pb (l)	28.451			
SiO ₂	45.815	0.02301		
CaCO ₃	82.341	0.04975		-1 286 998
CaO	41.84	0.02025		-451 872
CaSO ₄	77.487	0.09192		-656 051
SO ₂ (g)	47.697	0.005916		-855 628
SO ₃ (g)	58.158	0.02552		-1 347 248
C	17.154	0.004268		-878 640
CO (g)	26.861	0.006966	-8.2 E-7	
CO ₂ (g)	25.999	0.04350	-1.48 E-5	
CH ₄ (g)	14.146	0.07550	-1.8 E-5	
H ₂ (g)	29.066	-0.00084	2.013 E-6	
H ₂ O (g)	30.359	0.009615	1.184 E-6	

ELECTROCHEMICAL CONSTANTS

Definitions

1 Coulomb = the quantity of electricity transported in one second by one ampere.

R = The Universal Gas Constant
= 8.3143 joules. gmole⁻¹. °K⁻¹

F = Faraday Constant is the amount of electricity required to deposit or liberate one gram equivalent of an element or ion.
= 96 500 coulombs.

Faraday Constant may be expressed as Electrochemical Equivalents as follows:

Element	Atomic Wt	Valency	Coulombs/g	Amp hours/kg
Cadmium	112.41	2	1717	477
Cobalt	58.94	2	3275	910
Copper	63.54	2	3037	843
Hydrogen	1.008	1	95 734	26 587
Lead	207.21	2	931	259
Manganese	54.94	2	3513	976
Nickel	58.71	2	3287	913
Oxygen	16.0	2	12 062	3351
Zinc	65.38	2	2952	820

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PREFACE

The production of zinc metal commenced on a small scale in India and China during or before the 14th century and in Europe during the 18th century. Early production methods were based on the use of a retorting process in which zinc oxide was reduced with carbon in a heated sealed vessel or retort. Zinc metal was vapourised and collected by condensation from retort gases. Improved versions of the batch retort were the sole means of production for over 100 years until the early 20th century when the electrolytic process was developed. Continuous retorting processes were also developed in the first half of the 20th century and the zinc blast furnace was introduced to commercial production in 1960.

At the beginning of the 21st century retort processes have almost completely disappeared and the use of the blast furnace or Imperial Smelting Furnace is waning. Production of zinc is now predominantly undertaken using the electrolytic process, which represents over 80 per cent of the world's output at the start of the 21st century. The form of the process is well established and may be regarded as a relatively mature technology. Improvement has been progressive and evolutionary through the use of improved controls and equipment rather than radical changes to the basic process chemistry.

Other pyrometallurgical processes for the recovery of zinc from low grade and secondary materials, such as fuming, have been employed since the early 1900s and are still important in zinc extractive metallurgy.

The purpose of this text is to summarise the broad configuration of these processes and the important aspects of their design and operation as a guide for metallurgists working in the industry. It is also aimed at outlining the alternatives available to handle different situations and the reasons why particular process options might be used.

Professional metallurgists and engineers entering the industry may understand the principles and details of individual parts of the process they have to manage, but often do not have the broader background covering the evolution of the process, the fundamental reasons for the configuration used, and the complex interactions between component parts of the process which make up an efficient whole. A broad appreciation can avoid decisions being made that address a narrow issue in part of the process, but have adverse ramifications on the total process. It is also important to appreciate the alternative technologies available to address particular problems and situations.

This work is thus an attempt to provide information leading to a broader understanding of the whole zinc metal extraction process, as well as the details of component parts of the major processes involved. Attention is given to the physical and chemical basis of the key processing steps used and to the technical and scientific reasons for the selection of those steps and the operating conditions. It by no means provides a complete and exhaustive discussion of all aspects of each process, but it is hoped that this volume can serve as a general reference and guide, as well as serving to stimulate inquiry into further details and in-depth evaluation of particular aspects of the various extraction and metal production processes.

The material is drawn from both the technical literature and from a long-term association with the industry, and in particular from an association with so many competent and experienced professionals over many years, from whom a broad appreciation of the technology in its total context was obtained. This is considered to be very important for the achievement of optimum practical outcomes and it is hoped that this text may help impart a greater breadth of understanding of the technology to others in the industry.

Much appreciation is expressed for the efforts of the technical review panel from The Australasian Institute of Mining and Metallurgy, particularly Dr Roderick Grant and Professor Douglas Swinbourne who applied great rigour in their critique and provided many valuable suggestions to improve the contents and make the text suitably comprehensive and readable.

R J Sinclair
Melbourne, May, 2005

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We would also like to thank The AusIMM Metallurgical Society for their assistance in reviewing and editing this volume prior to publication.

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1986	1/86		*	13th Congress The Council of Mining and Metallurgical Institutions, Singapore, 6 Volumes
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	6/90		*	Sir Edgeworth David Memorial Oration, May 1990
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	1/91		*	Fourth Mill Operators' Conference, Burnie Tas, March 1991
	2/91		*	World Gold '91, Cairns Qld, April 1991
1991	3/91			Mining Industry Optimisation Conference, Sydney, June 1991
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	5/97	*	Contract Operators' Conference, Brisbane, Qld, October 1997
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	7/97		Mindev 97 - The International Conference on Mine Project Development, Sydney, November 1997
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	1/98	*	MINEFILL '98 - The Sixth International Symposium on Mining with Backfill, Brisbane, Qld, April 1998
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	3/98	*	Seventh Underground Operators' Conference, Townsville, Qld, June/July 1998
1999	4/98		Mine to Mill Conference, Brisbane, Qld, October 1998
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	8/2002	Value Tracking Symposium, Brisbane, Qld, October 2002
2003	1/2003	Twelfth International Symposium on Mine Planning and Equipment Selection, Kalgoorlie, WA, April 2003
	2/2003	Young Leaders 2003, Brisbane, Qld, April 2003
	3/2003	Sixth International Conference Acid Rock Drainage, Cairns, Qld, July 2003
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