Towards Understanding the

LEAD BLAST FURNACE

Reflections on research at the Port Pirie smelter and other studies

Spectrum 22

By Denby Ward

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THE MINERALS INSTITUTE

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Front cover image:
Lead blast furnace at Port Pirie. Courtesy of Nyrstar.
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Foreword

By their past reading of technical literature, some readers may be familiar with the work of TRA Davey[1] and his prescient words, now some 25 years old:

> *Although the blast furnace has been a faithful workhorse for many centuries, and one would be rash to predict its near demise, it is difficult to resist the conclusion that it must gradually give way to the next generation of small, intensive reactors which require neither the expensive sintering of feed materials, nor the production of metallurgical coke – both difficult to conduct in a pollution-free manner.*

The blast furnace has been a tool for the extractive metallurgist over many centuries and in that time it has become vastly more efficient as generations of practitioners applied their creative and scientific minds to the task of its improvement. In the past century the advanced standards of education and communications have accelerated the rate of improvement in all areas of extractive and process metallurgy. Despite this vast sweep of time and all the great tools that we now have at our disposal for plant measurements and data processing, I have yet to meet a person bold enough to claim that they thoroughly understand a lead blast furnace.

It is, I think, with this in mind that Denby Ward has written this remarkable book and chosen its title. Readers will recognise at once that this text is the collation of knowledge acquired over many decades, followed by much time spent methodically thinking of ways to distil its essence and present the ideas of most value in an accessible way. The field of extractive metallurgy is advanced by such effort, and this is all the more important for a technology that does not lend itself readily to many of the comforting assumptions that might normally be expected to simplify the life of a metallurgical engineer, such as plug flow, perfect mixing, thermal equilibrium and so on. Quantitatively describing the behaviour of the lead blast furnace is a task made more challenging when assumptions of such simplicity cannot be justified.

Even if many readers suspect that a proliferation of modern bath-smelting technologies has partially usurped the role of the lead blast furnace, there are at least two good reasons why it will remain part of the world's active lead-smelting technologies for some years into the future:

1. The lead blast furnace is very good at simultaneously producing slag with low lead content and dust with low zinc content; this is a feat many bath-smelting technologies struggle to attain.
2. The lead blast furnace has in the past been at its most productive when treating lead sinter, but this does not mean that a possible demise of lead sinter plants will inevitably leave the lead blast furnace stranded. The use of blast furnaces in the secondary lead industry has been commonplace for many decades, and there has been active exploration in recent times of the role of the lead blast furnace in primary lead smelters for the treatment of lead-rich slags from bath smelting. (A concept evaluated in Mount Isa in

the 1980s that has since met with noteworthy success in the lead industries of China[2,3] and Kazakhstan[4].)

The non-ferrous extractive metallurgical industry has often lagged a couple of decades behind the ferrous industry. This is true for both scientific and engineering endeavours such as the use of tonnage oxygen to enrich the blast air of a furnace, the automation of tapping and sampling equipment and the careful management of coke quality. This book does much to address the time lag when it comes to the science of the lead blast furnace. A generation ago, it was a learning experience for young metallurgists to read Biswas's fine book on the iron blast furnace[5]. The metallurgical and thermodynamic principles of the furnace were revealed and the observed behaviours were demystified and explained with clarity and logic. Readers of *Towards Understanding the Lead Blast Furnace* may in future come to think the same.

Alistair Burrows

Principal Metallurgist, Glencore Technology

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About the Author

Denby Harcourt Ward FAusIMM, FIEAust, CPEng (Ret), ME (Met & Chem, Adel.)

A graduate in Metallurgical and Chemical Engineering at the University of Adelaide, Denby Ward commenced a 30-year career in 1956 in lead process metallurgy via a postgraduate studentship at the University of Adelaide sponsored by The Broken Hill Associated Smelters Pty Ltd (BHAS). After transferring to the research department at their Port Pirie smelter in 1958, he completed a Master's degree by thesis on this project.

Successive promotions followed, eventually leading to General Manager positions in operations then redevelopment. Transferring to Melbourne with CRA Ltd in 1987, Denby took up a consultative/management role in research and development of process technology. He retired from CRA in 1992.

Following retirement, Denby acted in an advisory role in postgraduate and post-doctoral research as an honorary Fellow of the Engineering Faculty at Monash University. A personal interest was to explore the application of equilibrium thermodynamics to high-temperature metallurgical systems using computer programs. He retired from this post at the end of 2000.

While at Monash, Denby formed a private consultancy company to specialise in the field of non-ferrous extractive metallurgy. Between 1994 and 2000, he undertook national and international projects involving the application of non-ferrous metallurgical theory to topics such as lead-zinc process technology, feasibility studies in the copper, lead and zinc fields and the processing of complex polymetallic deposits, as well as acting as an expert in several legal proceedings. Denby wound up this company in 2000, but has since taken on work in a private capacity.

In studying both traditional and potential technologies for primary lead smelting and the ancillary processing of its products, Denby has travelled widely throughout the world, including remote areas of the Soviet Union, visiting other industrial and research establishments. He has served as an honorary member of steering and review committees for the GK Williams Laboratories at the University of Melbourne, and the CSIRO Division of Mineral Chemistry.

Acknowledgements

A few years ago, the subject of this book was suggested to me in my retirement by my long time friend and colleague Dr Rod Grant as a possible publication in the AusIMM Heritage Series. About the same time my interest had been further sparked by discussions with our mutual friend Dr Rod Sinclair during the preparation of the chapter on lead blast furnace smelting in his comprehensive book *The Extractive Metallurgy of Lead,* published by the AusIMM in their Spectrum Series. Since that time my text has vastly expanded beyond its original intention, but both friends have given me valuable assistance by way of suggestions and criticism in developing and organising the interlinked evidence and argument presented herein. I thank them most sincerely.

This book derives to a major extent from my 30 years of involvement in research, development and management experience at the Port Pirie works of the Broken Hill Associated Smelters. I am hugely grateful for the opportunities for my personal development there as part of a small but dedicated and successful research team vigorously interacting with highly professional operations staff. The opinions that I give here recall much discussion and debate with many people over many years. A few formal BHAS technical reports and memoranda still survive in my personal papers and form part of the basis for this book. To my colleagues from the Port Pirie years – many thanks for your dedication. There are too many of you to name personally. However, I would like to mention with gratitude particular mentors who provided the incentive and discipline for the development of a very callow Chemical Engineering graduate from the late 1950s onwards; John Lumsden and TRA (Ron) Davey, both giants in the world of theoretical metallurgy, who took the time to explain the detailed reasoning behind their astonishing mental leaps in the application of thermochemical principles; Don Blaskett, a hard taskmaster in experimental design and the logical evaluation of results, later a friendly guardian in the politics of dealing with senior management; Hans Zwillenberg, librarian extraordinaire, who taught me the value of observations from historical technical literature, the wealth of information to be found in the wider metallurgical literature and the value of developing sufficient skill to be able to read technical literature in its original language.

In conclusion I would like to extend my sincere and grateful appreciation to my editor, Kelly Steele of the AusIMM staff, who has spent many hours learning to understand the complex technical arguments contained in this work and has made many constructive suggestions to improve its grammar, logic and general presentation.

Denby Ward FAusIMM

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Overview

This work explores, in roughly chronological order from the 1950s onwards, development in the understanding of the physical and chemical phenomena governing the industrial operation of the lead blast furnace. Such development has involved the application of the evolving science of metallurgical thermochemistry in elucidating the behaviour of high-temperature multiphase and multicomponent systems, new instrumentation technology and analytical methods; these have been combined with the use of computers for complex analysis and modelling of production and research data. While based on the writer's 30 years' experience in research and management at the Broken Hill Associated Smelters Pty Ltd (BHAS) Port Pirie smelter until 1987, subsequent published sources are also drawn on for further illumination of the carbothermic reduction behaviour of the Pb–Zn–Fe–S–O slag system common to both lead and zinc blast furnaces.

Discussion begins with a résumé of the thermochemistry of the carbothermic reduction of reducible metal oxide species – specifically those of lead, zinc and iron – involved in reactions in the lead blast furnace. Particular reference is made to the significance of zinc oxide reduction, which at smelting temperatures produces zinc in vapour form.

Conjectural theory of state-of-the-art lead blast furnacing at Port Pirie in the 1950s is then discussed, leading into the reasoning behind the development of a thermochemical model of the process. This followed the successful commissioning, in the 1950s, of the Imperial Smelting process for the simultaneous production of lead and zinc in a single blast furnace, based on a detailed thermodynamic analysis of the competing reduction chemistries of the zinc and iron systems. Conditions were identified under which zinc was vaporised and subsequently recovered by condensation while iron was directed as oxide to a slag. The more easily reduced lead provided a separate and economic metallic by-product from the furnace. As a result of joint studies between Imperial Smelting and BHAS at Port Pirie, a related thermochemical model was developed to describe the higher oxidation potential operation of the lead blast furnace in which lead metal was the major product, with zinc and iron reporting to the slag. This model, entitled in this work the 'Lumsden model' after its author, provided a logical explanation of many of the unusual features and limitations experienced in the industrial operation of the Port Pirie lead blast furnace, and strongly influenced the direction of further blast furnace research.

The Lumsden model envisaged a division of the furnace's vertical temperature gradient, from the hearth upwards, into zones characterised by reactions with different modes of rate control:

- A slagging zone comprising tuyere and phase-separation functions in which chemical and thermal equilibrium was achieved between the gas phase and molten discharge products at a calculated temperature and oxygen potential consistent with operational outcomes.
- A zone of decreasing gas temperature and rising charge temperature characterised by the limiting rate of reaction between the CO_2 content of the rising gas and carbon in

the charge to form CO, but with thermal and chemical equilibrium maintained between reaction products.

- An upper reaction zone in which all reduction of oxidised lead compounds took place under an assumed mode of kinetic control. Lacking experimental data relating to the kinetics of such reduction, the assumed mechanism was that the rate of mass transfer to and from the charge surface was limiting and could be directly related to the rate of heat transfer. This allowed a mathematical solution that enabled a simulation of both phase compositions and temperature gradients in the upper furnace.

The circulation of reduction products volatilised in the equilibrium zone and subsequent re-oxidation higher in the furnace, combined with the effect of the exothermic reduction of oxidised lead, was shown to result in a release of thermal energy within the charge column, which could be offset only by the energy required for charge heating and, to some extent, by the endothermic gasification of the coke. Accordingly, the zonal heat balances afforded by the model showed there was an upper limiting ratio of PbO to slag constituents of the input sinter for successful operation at a given smelting rate. Otherwise, excess energy could be dissipated only in the form of the sensible heat of exit gases at elevated temperatures (locally described as 'hot top') and chemical energy in the form of CO. Operating the lead blast furnace therefore became a matter of meeting the physical and chemical requirements of the process while minimising the potential economic disadvantages of excessive coke consumption and restricted throughput resulting from premature fusion and bridging of the charge components. Although the model offered an explanation for most of the characteristic difficulties of operating the Port Pirie lead blast furnace, the extensive nature of its assumptions led to further field and laboratory research rather than immediate acceptance of proposed alternative modes of furnace operation. Reconciliation of the assumptions inherent in the Lumsden model with subsequent research findings now allows a better understanding of lead blast furnace chemistry.

The equilibrium premise is examined in light of subsequent investigations. Its continuing validity is demonstrated by consistency with several independent measures of the oxygen potential from zinc partition data and oxygen potential probe, consistency between calculated and measured lower furnace heat balances, analogy with the Imperial Smelting Process and the ability to explain, by extrapolation, other thermochemical phenomena peculiar to the lead blast furnace (such as the formation of zinc sulfide accretions in the hearth and lower wall zones also discussed in this work).

Apparent anomalies in the determination of the oxygen potential from the lead oxide content of the slag are discussed. It is now accepted that all industrial slags contain a variable quantity of entrained metallic lead along with the dissolved PbO. Conventional rapid analytical methods used in the industry to determine the residual lead content in slag do not permit differentiation between the two species. The consequent determination of the activity coefficient of PbO in industrial slag requires the use of sophisticated and laborious analytical methods to differentiate between entrained metal and residual PbO. It is therefore not directly possible to arrive at a prediction of the oxygen potential from a conventional analysis of the total residual lead in slag as assumed by Lumsden; nor, conversely, is it possible to unambiguously predict the residual lead content in lead blast furnace slag from a knowledge of the oxygen potential.

A key outcome of the assumption of equilibrium between gas and charge components at a defined oxygen potential and temperature low in the furnace is that the rising gas stream contains not only combustion products but also volatilised PbS and zinc vapour. The reduction and volatilisation of ZnO to zinc vapour is highly endothermic and represents a major extraction of thermal and chemical energy from the equilibrium zone into the rising gas stream. As a result of the decreasing temperature of the rising gas stream and its reaction with the reducible oxides in the descending charge, the PbS and zinc vapours revert to Pb, ZnS and ZnO, with consequent changes to the CO_2/CO ratio and the release of exothermic heat to the charge. Heat transfer between rising gas and descending charge therefore depends not only on physical heat transfer considerations, but also (and very significantly) on thermochemical effects governed by mass transfer. Exactly where in the furnace the major heat transfer events might take place has an important bearing on the softening and fusion behaviour of the charge – the traditional cause of gas permeability constraints and resultant production limitations in the lead blast furnace. The Lumsden model arbitrarily assigned these effects to one or other of the assumed reaction zones in order to arrive at a mathematical description of Port Pirie furnace behaviour, which could be extended to derive a presumed mechanism of charge fusion and bridge formation. Subsequent investigations at the Chimkent smelter in the then Soviet Union and at the Belledune smelter in Canada refute the Lumsden model assumptions for the upper furnace chemistry and point to a much more complex system with overlapping reactions between temperature zones.

On this later evidence, it is postulated that the furnace charge column can be envisaged as three contingent and possibly overlapping zones characterised by the physical state of the non-coke fraction. From the stockline downwards:

- The upper reduction zone – a solid-state zone in which all reduction takes place by a chemically controlled reaction between the gas phase and the oxide phases PbO and lead ferrite. Charge temperature gradient is 25–850°C.
- The lower reduction zone – a mixed-mode heat and mass transfer zone characterised at lower temperatures by the reduction of molten lead-bearing silicates supported within a lattice-like structure of high-melting melilites and spinels; at higher temperatures coke starts to be consumed by gasification reaction with CO_2, while liquid-phase reduction continues and slag formation commences. Charge temperature gradient is 850–1150°C.
- The equilibrium zone – encompassing a slagging zone comprising tuyere (coke combustion by air injection) and phase separation functions. Equilibrium temperature of all phases is 1150–1200°C.

Such a division retains the Lumsden concept of a thermochemical equilibrium that explains the consistency of the outcomes of smelting, both within and between operating sites, in respect of product temperatures and compositions given the known physico-chemical limitations and vagaries of the carbothermic reduction process in the column of a lead blast furnace.

In this light this work examines:

- the effect of physical changes; that is, the softening caused by fusion of low-melting charge constituents resulting in compaction of the furnace column and hence a decrease in gas permeability, deleterious to coke combustion rates and hence furnace productivity, resulting from the chemical constitution and structure of the input sinter
- the influence of reaction kinetics on the chemistry of the carbothermic reduction of lead sinter.

Several studies have attempted to relate the course of reactions down the vertical temperature and composition profiles of the lead furnace to the results of limited vertical gas sampling and temperature traverses. These have little general validity in that the gas temperature and composition have been shown to vary quite rapidly and unpredictably with time and location within the horizontal cross-section at any particular level in the furnace. Secondly, such probes provide no information as to the solid/liquid-phase structure, temperature or composition of the sinter charge. Thirdly, and most importantly, the composition of any sample of a gas with a significant content of zinc vapour changes within the sampling train – by reason of the reversion reaction during cooling between zinc vapour and CO_2 to form CO. Such gas analyses are therefore invalid and potentially misleading.

Pilot-scale studies at the Chimkent smelter in Kazakhstan and studies on the operational furnace of the Belledune smelter in Canada have provided useful insights as to the progress of reduction within the charge. Both showed that the reduction of the various forms of oxidised lead compounds took place at different rates and different temperatures down the charge profile. In each case, laboratory-scale experimentation followed in attempts to describe the outcomes of reduction. This work was superseded by the extensive electron microprobe analysis of Belledune sinters indicating the chemical and physical complexity of the phase structures, many of which were solid solutions with varying proportions of reducible lead, iron and zinc. A corollary of these findings is that, as the solid phases melt, the composition of the molten phase changes in an unpredictable manner – both by the increment of new melt of unknown composition as well as by reduction. The composition of the reducible phase in the lead blast furnace is therefore completely unknown at any point and any temperature within the lower reduction zone.

The deportment of sulfur in the lead blast furnace is of major metallurgical and economic significance, relating both to the operation of the blast furnace itself and to subsequent by-product recovery operations. Occurring in the sinter feed in both sulfide and sulfate forms, it exits the furnace in both slag and bullion products and as SO_2 in the exit gases. Under certain circumstances it can form ZnS-rich accretions in the hearth, on the side walls and in the centre of the furnace. Historically, the growth of such accretions was campaign-limiting and although a certain amount of sulfur in feed could be tolerated, the development of the sintering process was generally aimed at minimising sulfur levels. On the other hand sulfur is required in the product bullion to optimise the subsequent recovery of copper and precious metals in refining operations. This work explores the thermochemistry of deportment of the sulfur content of sinter within the blast furnace and potential methods for its control.

Recent revisions of thermochemical data relating to the partition of sulfur between slag and bullion now allow an understanding of the formation of deleterious sulfidic accretions in the hearth and on the side walls of the lead blast furnace. Equilibrium mechanisms now explain why there is an upper limit to the amount of sulfur eliminated in the slag and bullion products, with any excess arising from the input charge leading to accretion formation.

Mass balances at Port Pirie during the period 1958–1987 consistently showed that 60–70 per cent of the sulfur entering with the various charge components reported to slag and bullion, the remaining excess being eliminated as SO_2 and in entrained fume components in the exit gases. The kinetics of shaft reactions forming SO_2 from input charge components are therefore an important consideration in furnace operation. The question therefore arises as to whether the overall control of sulfur deportment can be exerted via the sintering process.

The chemistry of the sintering process is revisited to show that by considering the behaviour of the reaction system as a molten liquid phase, the deportment of sulfur between exit gases and molten phases within the reaction band of the raw material bed on the sinter machine can be inferred from the thermochemistry of the Pb-S-O system at sintering temperatures, oxygen and sulfur potentials. Successfully achieving desirable physical and chemical properties in product sinter via combustion reactions in the sinter bed requires careful control of many operational variables to achieve consistent, continuous reaction conditions of mass balance and temperature. If physical sinter properties are the main determinant of blast furnace productivity (a long-held opinion at Port Pirie), it can be concluded that sinter sulfur content and/or sulfate/sulfide ratios are not independently controllable parameters other than within broadly defined limits.

The mechanisms of the endothermic evolution of SO_2 from sulfide- and sulfate-bearing sinters in the blast furnace have been studied in light of the reaction of the oxide species PbO and $PbSO_4$ with the reductants PbS and CO. The deleterious effects of battery scrap addition to the operation of the Port Pirie blast furnace were clearly identified, and despite the potential economic advantage, the practice was subsequently discontinued.

Discussion then proceeds to the possibility of modelling the lead blast furnace process. Physical properties of the sinter have been demonstrated by statistical analysis to have a dominating effect on blast furnace productivity. The causes are understood but such physical properties such as melting and softening behaviour are also related to the chemical makeup of the sinter and the intensity of the sintering process, the outcomes of which are unpredictable and cannot be evaluated. Regardless of productivity, however, the heat balance of a furnace must always hold. Economic factors such as Pb/C and slag/C ratios, together with environmental heat losses, reflect the efficiency by which the balance between the heating and reduction requirements of the coke fuel can be managed. The question is whether the thermochemistry blast furnace operation can be rigorously modelled to allow simulation and optimisation of current practice.

For the purposes of discussion, the course of reaction is considered relative to the three reaction zones proposed and following the Lumsden model approach of considering the consequences of combustion in the equilibrium zone on a per mole of carbon basis. It is shown that boundary conditions relating to the temperatures and compositions of both descending charge and rising gases in each of the three zones can be derived by calculation from operational data.

Modelling of the upper reaction zone by considering only the outcome of reduction of solid-state charge components allows the definition of composition and temperature boundary conditions between upper and lower reduction zones at a charge temperature of 850–900°C. The boundary conditions between equilibrium and lower reduction zones at a temperature of 1150–1200°C are those derived by the Lumsden model. The task of modelling the lower reduction zone covers the transition from solid- to liquid-phase reduction of reducible charge components at the top to the outlet of fully reduced molten products at the base.

Kinetic parameters (energy of activation, rate constants) relating to the reduction of molten lead-bearing slag melts by carbon monoxide have been tabulated in the literature for all individual systems involved in lead smelting. While these were determined in the context of modelling carbothermic reduction in the Kivcet process, they should also be valid for the lead blast furnace. However, the equation for evaluating the rate of heterogeneous reduction of a molten phase by a gas requires a knowledge of the interfacial area for reduction by the blast gases, the thermodynamic activities of the reducible species, the partial pressure of the reduction gas and the temperature of the reducible phase. No unambiguous methods for determining the charge and gas phase temperature and composition profiles in the lead blast furnace have yet been devised. It is concluded that there is still no completely valid basis for quantitative dynamic modelling of the lead blast furnace process.

Discussion concludes with a further consideration of the fact that residual lead reporting to slags from primary lead smelting processes exists in both oxide and metallic forms.

The dissolved oxide is a necessary product of the slag's equilibrium thermochemistry at the temperature and oxidation potential of the process. In the case of the lead blast furnace, the separately identifiable metallic lead phase in the form of small droplets can amount to as much as 70 per cent of the residual lead content of the slag. Laboratory studies, together with field evidence that the residual lead content of slags varies with furnace geometry and throughput rates (that is, slag residence time within the furnace), suggest a phase-separation phenomenon based on sedimentation rates of lead droplets. Calculation of molten slag sedimentation rates of lead droplets of a size observed in many micrographic studies yields values of several minutes to several hours per centimetre under static conditions. Under turbulent conditions, and particularly in bath smelting processes involving high-shear gas injection, it is possible that such droplets may not separate at all. Laboratory evidence is cited to show that a fivefold variation in the viscosities of 30 industrial slags has been reflected in a fivefold variation in residual lead content in the slag, so supporting the contention that a sedimentation mechanism is important in determining droplet retention of metallic lead in discharge slag.

The possible causes of the generation and retention of such droplets are discussed. Micrographic examinations of partially reduced sinter incidental to several laboratory-, pilot- and industrial-scale investigations show lead droplets entrapped within the supporting high-melting lattice structure. The suggested mechanism of formation is by gaseous reduction at the phase boundary of liquid lead silicate glasses held within the lattice. What might happen to such droplets after full slag formation is necessarily conjectural. An alternative mechanism involves the homogeneous reduction of oxidic lead within the liquid phase via electronic transfer, effectively by ferrous iron species. No interfacial contact between dissolved oxidic lead and the gas phase is necessary. Such a mechanism on an ionic scale requires some mechanism of coalescence to form separable droplets, but potentially such metal could be very finely divided.

Such discussion leads into further consideration of mechanisms of coalescence of droplets within a two-liquid-phasesystem, pointing out that an effective separation of metallic lead from quite viscous slags has been achieved in other processes with other configurations. Usually this involves providing extended settling times, gentle agitation and/or contact with a third solid phase. None of these seem applicable to enhancing phase separation within the geometry of the lead blast furnace.

Introduction

1

This volume's intention is to chart the gradually evolving understanding of the interrelated physical and chemical parameters controlling the operation of the lead blast furnace, particularly the Port Pirie blast furnace. Except where relevant to a particular matter, it is not intended to provide a general description of the operation, equipment, engineering, environmental performance, capacities or economics of the sintering/blast furnace process as applied in commercial lead production. These matters are comprehensively discussed and annotated in section B of Sinclair (2009).

Technical literature relating to the chemistry of the lead blast furnace has been limited for two major reasons. First, the chemistry of the process is complex, involving the interacting reduction chemistries of three elemental metal species (lead, zinc and iron), carbon combustion, the behaviour of residual sulfur species, internal volatilisation and condensation cycles, the deportment of minor but economically important metals, heat and mass transfer influences, slag chemistry, phase separation issues and the like. Second, it was and still is very difficult to obtain meaningful experimental data from furnaces fully encased in steel water jackets and possessing an aggressive internal environment, which leads to early failure of measurement probes. While inputs to the furnace can be metered, instruments capable of measuring such basic output criteria as metal, slag and off-gas temperatures, flow rates and compositions only became available from the 1960s onwards. No simple method of measuring the temperature gradient of solid materials within the descending charge has yet been devised. Techniques for sampling high-temperature products have always been questionable because of the potential for phase separations with consequent composition changes during cooling from a molten state. Even with the evolution from the simple stoichiometry of the early 20th century to the current inventory of thermochemical databases, instrumentation and computerised techniques – not to mention a century of laboratory investigations and operating experience – there is still no unambiguous interpretation of all the vagaries of lead blast furnace behaviour.

At best, this volume presents a subjective viewpoint of the current state of the art.

2

Carbothermic Reduction of Metal Oxides

The basic chemical expression for the carbothermic reduction of metals is:

$$2MeO + C \rightarrow 2Me + CO_2 \tag{2.1}$$

The effective mechanism of reduction, however, is through the agency of carbon monoxide.

This is formed at elevated temperatures, both by the reaction of initially formed carbon dioxide with additional carbon and by a cyclic reversion of the carbon dioxide produced by the reduction reaction:

$$C + O_2 \rightarrow CO_2 \tag{2.2}$$

$$CO_2 + C \rightarrow 2CO \tag{2.3}$$

$$MeO + CO \rightarrow Me + CO_2 \tag{2.4}$$

Equations 2.1 to 2.4 represent a combination of endothermic and exothermic reactions that result in a mixture of product metal and carbon-bearing gases. To give an overall heat and mass balance the outcome can be expressed as:

$$MeO + (1 + x + 2y)C + (x + y)O_2 \rightarrow Me + xCO_2 + (1 + 2y)CO \tag{2.5}$$

The rate at which reaction (Equation 2.3) can take place is dependent on temperature conditions and becomes insignificant in the process chemistry below about 1000°C. Thus, effective use of carbon as a reductant requires that operating temperatures be maintained above 1000°C, and the product gas from reduction reactions will contain a mixture of CO and CO_2 subject to the kinetic and equilibrium constraints of Equations 2.2 to 2.4. Reduction by CO may still take place below that temperature, but as required by Equation 2.4 the only product gas can be CO_2.

Equation 2.5 implies that a successful carbothermic reduction of an oxide ore to metal and waste slag requires carefully managing the relative inputs of charge, fuel and blast oxygen to achieve the appropriate output mass and energy balances. Over the last century, such a process has been traditionally achieved in a blast furnace. Input material is fed to the top of a column of charge consisting of solid oxides, fluxes and coke fuel. At its base, air is blown into a bed of incandescent carbon fuel (coke) at a temperature sufficient to generate a reducing gas mixture consisting of nitrogen and carbon oxides. This hot gas mixture then rises counter-current to the descending charge of oxide ore and coke, raising the temperature of the charge to the reaction temperature and reducing the oxide to metal. The products tapped at the base of the furnace are molten metal and a molten non-metallic slag formed by the addition of suitable fluxes to combine with the impurities from the ore and coke.

In practice, reaction temperatures and product outlet temperatures and compositions fall into specific ranges for the metal being smelted. This follows partly from the melting points of the product slag and metal, and partly from the thermochemistry of the metal oxide being reduced. The equilibrium constant K for reaction (Equation 2.4) is characteristic for a given metallic element at a given temperature and is represented by component activities in the general equation:

$$K = \frac{p_{CO_2} \cdot a_{Me}}{p_{CO} \cdot a_{MeO}} \tag{2.6}$$

For oxide and metal in their pure solid or liquid states, both a_{Me} and a_{MeO} have a numerical value of 1. If the gas component activities are represented by their partial pressures (atm), the equilibrium Equation 2.6 reduces to:

$$K_{2.7} = \frac{p_{CO_2}}{p_{CO}} \tag{2.7}$$

This means that the reduction of a pure metallic oxide to metal at a given temperature can only take place at a CO_2/CO ratio below that represented by the value of the equilibrium constant. Characteristic equilibrium constants for the reduction of metal oxide species are readily obtainable from thermodynamic databases; for example, at 1200°C:

$$\mathrm{FeO} \rightarrow \mathrm{Fe}, K = 0.348; \mathrm{ZnO} \rightarrow \mathrm{Zn(gas)}, K = 0.328;$$
$$\mathrm{PbO} \rightarrow \mathrm{Pb}, K = 414; \mathrm{CuO} \rightarrow \mathrm{Cu}, K = 3.633 \cdot 10^4$$

Metal oxides such as those of iron, which have several oxidation states, also have equilibrium CO_2/CO ratios at which a sequential reduction of the oxides can take place; for example:

$$\mathrm{Fe_2O_3} \rightarrow \mathrm{Fe_3O_4} \rightarrow \mathrm{FeO} \rightarrow \mathrm{Fe}$$

Equilibrium values at 1200°C for the various reductions are:

$$\mathrm{Fe_2O_3} \rightarrow \mathrm{Fe_3O_4}, K = 4.672 \cdot 10^4; \mathrm{Fe_3O_4} \rightarrow \mathrm{FeO}, K = 1.747; \mathrm{FeO} \rightarrow \mathrm{Fe}, K = 0.348$$

Now consider the reaction:

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} \tag{2.8}$$

for which the equilibrium constant is:

$$K_{2.8} = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{1/2}} \text{ and } p_{O_2}^{1/2} = \frac{K_{2.7}}{K_{2.8}}$$

The oxygen partial pressure p_{O_2} is a simple function that is easily calculated from standard thermodynamic tables. In technical literature, the values $RT\ln p_{O_2}$ – usually referred to as the *oxygen potential* or, alternatively, $\log_{10} p_{O_2}$ – are often used interchangeably with the characteristic CO_2/CO ratio to describe the reducibility of different oxides.

Primarily as a result of the differences in the oxygen potentials for their reduction by carbon, the different metals have different temperature and thermochemical requirements to achieve effective economic recovery. This results in markedly differing configurations in the furnaces used in each case. From antiquity, raw materials containing the oxides of iron and lead and, more recently, zinc have been smelted by the blast furnace process. Whereas the iron blast furnace treats oxide ores largely free of impurities, both the lead and zinc blast furnaces treat oxidised materials derived from sulfidic concentrates. Such concentrates are recovered from complex orebodies containing intergrown sulfide species of several metals. The extent of concentration and separation of individual sulfide minerals achievable by ore dressing methods varies from orebody to orebody. Thus, after oxidation of the sulfide concentrates to a sintered agglomerate, zinc furnaces produce metallic zinc and copper-bearing lead products, together with an iron-rich slag. Lead furnaces typically produce copper-bearing lead together with an iron- and zinc-bearing slag. In each non-ferrous operation the interacting reduction behaviour and consequent deportment of three major reducible oxides – iron, zinc and lead – must therefore be taken into account. Copper, the most easily reduced of the non-ferrous metals and readily soluble in lead bullion, has little bearing on the reduction chemistry in zinc and lead blast furnaces.

From this consideration of the basics of carbothermic reduction chemistry, it is not immediately apparent that a separation of zinc from iron by carbothermic smelting should be possible. A simple comparison of the equilibrium CO_2/CO ratios listed suggests that metallic iron should be the product before zinc; however, at smelting temperatures elemental zinc would be in vapour form, and the contribution of zinc vapour to the total atmospheric pressure at smelting temperatures (its partial pressure equating to a_{Zn}) cannot have a value of 1, but is lower because of the presence of CO_2, CO and N_2 arising from the reaction between the input blast and incandescent coke in the charge. The value of the CO_2/CO ratio in Equation 2.6 must therefore be raised to maintain the value of K, allowing the preferential reduction of ZnO before that of FeO. Recognition of this fact, as described by Lumsden (1971), gave rise to the development of the Imperial Smelting process for the production of zinc by carbothermic reduction in a blast furnace. For the same reason, it might appear that reducing zinc oxide species is improbable at the high CO_2/CO values at which the reduction of lead can be successfully achieved. In practice, zinc can be and is reduced in the smelting zone of the lead blast furnace to produce a zinc vapour product present in the furnace atmosphere at low but significant partial pressures.

From this analysis, it would appear that the lead blast furnace process should be a readily accomplished separation of easily reduced lead metal from major accompanying metals reporting as oxides in the slag. In practice, the development of stable economic operating practices has proved to be far from simple. In both the lead and zinc blast furnaces, iron species are used as fluxes in the constitution of the discard slag. The slags in both processes contain reducible oxide species of iron, residual lead and zinc, so that the slag is not just a collector of inert gangue minerals but an active participant in the reduction chemistry. The values of the thermodynamic activities, a_{MeO}, of the different metal oxide species in the slag must therefore be considered when understanding the outcomes of these processes. A further complication is the profound effect of the volatilisation and subsequent condensation of zinc and lead species on the heat balances and temperature distributions within the furnace. In the lead furnace there are additional complications due to the presence of residual sulfur in the furnace feed, an inevitable outcome of the chemistry of the Pb-S-O system underlying the sintering process used for the oxidation of lead sulfide concentrates. The formation of refractory sulfidic accretions in and near the hearth of the lead blast furnace has long been recognised as a major factor limiting operating-campaign life. The volatilisation of PbS is another factor in the reduction thermochemistry.

3

Lead Blast Furnace Smelting

Historically, the lead blast furnace was resurrected as the preferred method for smelting oxidised ores from discoveries of massive silver-rich deposits in remote areas of North America and Australia in the late 19th century. At that time European practice had evolved to allow the treatment of sulfidic materials, which were smelted by a combination of hearth roasting and reverberatory furnace reduction. As mining of New-World discoveries proceeded into underlying sulfide orebodies, these rudimentary lead blast furnaces ran into treatment difficulties predictable from earlier experience. The survival of the lead blast furnace as the preferred means of reduction to produce lead bullion was ensured, however, by the almost simultaneous discovery of flotation as a means of concentration and separation of lead and zinc sulfide concentrates, and the invention of the Dwight and Lloyd sintering machine as a means of roasting and agglomerating fine-grained lead sulfide concentrate, together with fluxes, into a self-fluxing massive form that simulated oxidic ores. This opened the way to developing even larger furnaces, which has been well described in metallurgical literature throughout the 20th century.

In general, early papers described developments in physical configuration and operating practice based on careful observation, rather than provide any theoretical explanation of the processes occurring within the furnace. These chemical processes were expressed in terms of simple stoichiometric equations without considering the thermal effects. While ‘equilibrium’ was occasionally mentioned, there could have been no real understanding of what this meant. The 20th century development of the lead blast furnace has been, in fact, concurrent with the evolution of metallurgical thermochemistry. Willard Gibbs had developed his ideas of thermodynamic equilibrium between reacting phases in the early 1870s, but it was only in the 1920s that Lewis and Randall successfully applied Gibbs’ principles to chemical processes. There was no real theory to assist in the development of lead blast furnace chemistry for several decades to come.

Iles (1902) and Dwight (1903) set down the desirable features of good lead blast furnace practice: direct recovery of lead as bullion, slag fluid and low in lead, top conditions cool and quiet, charge descending uniformly over the shaft area, furnace free from serious accretions and good furnace speed. A reading of their papers reveals that, in practice, only some of these outcomes were achieved, and only then for limited periods. Dwight also set down five factors that controlled reduction in the lead blast furnace:

1. chemical composition of the furnace charge
2. proportion and characteristics of the fuel
3. air volume and pressure
4. dimensions and proportions of the furnace
5. mechanical character and arrangement of the smelting column.

The main problem in defining how these variables influenced overall performance of the furnace lay in how each affected one or more other performance criteria, often to conflicting extents. Thus it was found that although the trend to larger furnaces alleviated or solved some of the more obvious problems encountered in the first small furnaces, there appeared to be practical limitations on the furnaces' maximum dimensions that could be satisfactorily operated.

Lead blast furnace practice today still conforms to these early principles – with the added constraints of environmental and occupational health regulations, as well as the need to optimise the downstream treatment of by-product metals and recover values from the resultant recycles. Certain operating problems and capacity limitations remain common to all plants, which can be summed up under these categories (not necessarily in order of importance):

- limited blast penetration resulting in variable tuyere zone chemistry and leading to different furnace/tuyere zone configurations
- formation of accretions (bridges, hangs) limiting the duration of operating campaigns
- charge segregation according to size and specific gravity
- variable coke performance and consumption
- lead losses in slag resulting from differences in slag chemistry and furnace configuration
- a tendency towards hot top operation.

Port Pirie Developments

4

The evolution of the unique Port Pirie blast furnace design from the 1920s onwards has been described by a series of Broken Hill Associated Smelters Pty Ltd (BHAS) staff, whose work was reviewed by Grant (2000). It is not the author's intention to discuss these developments except to illustrate where they interrelate with the process chemistry and, consequently, furnace performance. While theories abounded, the state of the art of metallurgical thermochemistry during the early period of investigation under G K Williams[1] was inadequate to provide anything other than a background to what was essentially engineering and practical operational development. In this field, the team's approach can be contrasted with their concurrent work on refining developments where inadequacies in theory were identified, rectified by laboratory and pilot-scale studies, and the results exploited in new processes or practice.

The first BHAS paper on lead blast furnace theory, by Haney and Hopkins (1954), was published many years after the double tuyere row furnace design at Port Pirie was well established in operation. Speculations were made based on observation of operating furnaces and outcomes of laboratory investigations into the chemical and physical factors affecting blast furnace performance. Their conjectures relating to the dual role of coke as both reductant and fuel were influenced by statistical findings that overall coke consumption could be optimised by suitably blending different size ranges of coke. By the late 1950s this had led to a concept of separate heating and reduction roles for the different coke size ranges in different parts of the furnace. Even at that time this idea was not in accordance with known carbon combustion chemistry. The paper recognised the adverse effect of charge softening on furnace throughput. Although, in retrospect, some of the ideas expressed by Haney and Hopkins were based on false premises, this paper marked the beginning of a long period of research at Port Pirie into the chemistry of processes occurring within the lead blast furnace. Grant (2000) describes some of the projects undertaken over the next two decades, facilitated by general advances in instrumentation and metallurgical thermochemistry. The availability of ever more powerful computers to carry out sophisticated multivariate statistical studies, thermochemical calculations and the physico-chemical/economic modelling of high temperature processes were utilised to better understand the apparently fickle behaviour of the lead blast furnace.

An early benefit of softening temperature/reduction experiments described by Haney and Hopkins followed the commissioning of the world-first updraught sintering machine at Port Pirie in 1956. Originally intended as a semi-industrial scale unit, the machine soon showed that not only was its sulfur elimination capacity efficient enough to avoid

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[1] G K Williams – a famous name in Australian metallurgical research and development. Williams commenced as a Research Officer in the BHAS Melbourne laboratories in 1919; he then moved to Port Pirie where he became Research Superintendent in 1925 and later General Superintendent in 1943. Although specialising in lead refining processes, Williams' teams were also active in blast furnace and sinter plant development. Potential processes for zinc recovery from slags and the direct smelting of lead concentrates were also the subjects of examination during the 1930s. Williams was later involved in the development of the zinc blast furnace by the BHAS sister company Imperial Smelting Co. A biography has been published by Andrews (1985). A listing of his patents and publications is presented by Grant (2000).

a second stage of sintering (as was the case with downdraught sintering), its production capacity was sufficient to meet the full requirements of the Port Pirie operation. The sinter appeared hard and well fused, but its blast furnace performance proved disastrous by comparison with the downdraught process. A major difference in the two processes – at first thought to be an operating advantage for the updraught version – was that there was little or no metallic lead-fall into the wind boxes of the updraught machine. The statistical studies reported by Haney and Hopkins had shown a correlation between furnace performance and the amount of lead-fall in the downdraught process. The cause of lead-fall was attributed to the roast reaction:

$$2PbO + PbS \rightarrow Pb + SO_2$$

taking place between the downward flow of molten-oxidised material ahead of the combustion flame front and the sulfide-bearing feed. This appeared not to occur in the updraught process. A trial was then carried out in which a quantity of up to 2.5 per cent coke breeze was added to the updraught sinter charge; this had been regular practice at Port Pirie in the two-stage downdraught technology. The introduction of coke to the updraught machine resulted in the production by carbothermic reduction of metallic lead, which was held within the sinter structure rather than falling out into the wind boxes. Such sinter, with a higher softening temperature, resulted in furnace performance exceeding the best previous levels achieved with downdraught sinter (Hopkins, 1958). Although a combined oxide lead content of less than 35 per cent in sinter (of a total of 45 per cent) fed to the Port Pirie lead blast furnace was set as a control level, later statistical work (Grant and Cunningham, 1971) showed that even lower combined lead levels in sinter could result in further improvements in furnace performance. A theoretical explanation for this outcome came early in the 1960s.

The late 1950s had seen the commissioning of the first industrial-scale zinc-lead blast furnaces using the Imperial Smelting process. The process is analogous to the lead blast furnace to the extent that it uses feed desulfurised and agglomerated on an updraught sintering machine and produces lead bullion and slag as hearth products. It differs from lead furnaces by producing metallic zinc by condensation of zinc vapour from the hot off-gases, which is facilitated by using a hot feed and a blast preheated by employing the fuel values inherent in the high CO content of the off-gases. In principle, both processes operate in different parts of the spectrum of the lead-zinc-oxygen-carbon system using a slag based on the iron oxide-silica-lime system. Although the Imperial Smelting Furnace (ISF) had been developed as a means of producing zinc with a small amount of lead by-product, it was claimed at the time that its operation could be extended to produce a majority of lead product while still producing zinc metal. This was of interest to BHAS as some six million tonnes of lead blast furnace slag had been accumulated at Port Pirie in the expectation of eventually finding an economically profitable method of recovering its high (approximately 17 per cent) zinc content. Although BHAS had experimented with other zinc recovery processes, in particular the slag fuming process, the remoteness of the Port Pirie site from suitable carbon reductant sources had been a significant economic deterrent to their being adopted. On the basis of claims for the performance of the ISF, BHAS became an early licensee of the process in the belief that it would offer a means of recovering the zinc content of recycled dump slag while maintaining high lead production rates. Subsequent disagreements between BHAS and Imperial Smelting over the theoretical fuel requirements of the projected modified process led to smelting trials of lead-based sinters in the experimental ISF at Swansea in Wales. The results of these trials showed that the higher residual sulfur levels in lead-based sinters compared with zinc-based sinters led to operating problems. Their solution incurred significant capacity and fuel penalties such that BHAS decided against proceeding with the project.

One consequence of the joint studies by Imperial Smelting and BHAS was an exchange of senior research personnel. This resulted in models of the thermochemistry of both the zinc blast furnace and the lead blast furnace, based on state-of-art metallurgical chemistry at the time and operating data derived from full-scale and experimental furnaces. Both models were the work of the eminent British pyrometallurgical theoretician John Lumsden, who spent nearly a year with the BHAS Research Department in Port Pirie. His model of the zinc furnace chemistry was eventually available in the public domain (Lumsden, 1971), but his concept of lead furnace chemistry still exists only in the form of an internal BHAS report (Lumsden, 1960); this is possibly because his approach was almost entirely inductive, using theoretical data from limited laboratory studies and mass and heat balance data from operational furnaces. Lumsden acknowledged that further experimental verification was required. Nevertheless, the model appeared to explain most of the phenomena associated with lead blast furnace practice as well as forming a basis on which much subsequent investigation at Port Pirie was based. It has always remained hypothetical, containing assumptions that were difficult to prove or disprove at the time but which now can be examined in light of later evidence, both from BHAS experiments and from the technical literature.

5

The Lumsden Concept of Lead Blast Furnace Chemistry

In both his 1960 and 1971 papers, Lumsden considered the physical chemistry of reaction between the counter-current rising flow of hot reducing gas generated by carbon combustion in the hearth zone and the downward flow of a charge consisting of metallurgical coke and self-fluxing oxide feed. This led to a concept of separate temperature zones involving different heat and mass transfer processes, brought about by chemical changes controlled either by kinetics or equilibrium thermodynamics and physical changes of state. Volatilisation of the charge or reaction product components was a consideration in both lead and zinc furnaces. Common to both models was the hypothesis that at some point down a vertical profile of the furnace there should be a zone in which the descending charge and rising reducing gas originally generated at the tuyere zone were essentially at the same temperature, and in which an approximation to both chemical and thermal equilibrium was attained. In each model, the outcomes of reaction in the upper furnace zones ultimately depended on the composition of the gases rising from the lower zones. Since there are considerable differences between the zinc and lead blast furnaces in respect to equilibrium zone temperature and oxidation potential – and charge column temperature profiles and heat and mass balances – the only common thread between the models is the application of Lumsden's assumed reaction mechanisms. Further discussion is therefore limited to the 1960 model derived for the lead furnace.

For the lead furnace, Lumsden postulated an underlying zone he termed the 'slagging zone'. Here, in the sequence of reactions, carbon first burned to a mixture of carbon monoxide and carbon dioxide under conditions determined by the mass balance of tuyere air and residual coke. A fully molten slag was formed from fully reduced charge materials descending from above that immediately reacted with the combustion gases. This led to the volatilisation of lead sulfide and zinc, thus modulating the gas temperature and setting up a system in which the gas and liquid phases were effectively in chemical and thermal equilibrium with each other. The relevant volatilisation reactions adopted for equilibrium calculations were:

$$\mathrm{ZnO(s)(slag)} + \mathrm{CO(g)} \rightleftharpoons \mathrm{Zn(g)} + \mathrm{CO_2(g)} \qquad (5.1)$$

$$\mathrm{ZnS(s)(slag)} + \mathrm{Pb(l)} + \mathrm{CO_2(g)} \rightleftharpoons \mathrm{ZnO(s)(slag)} + \mathrm{PbS(g)} + \mathrm{CO(g)} \qquad (5.2)$$

Lumsden argued that not only was such a system theoretically feasible, but that heat and mass balances of such a zone at a temperature approximating that of the final slag and bullion were consistent with operational measurements. The temperature of the equilibrium was calculated by heat balance from operating data averages to be about 1150°C, while the equilibrium CO_2/CO ratio in the reaction gases was calculated from component activities in slag and bullion to be 4:1. (Later thermodynamic data and laboratory investigations of slag chemistry now suggest the ratio to have been 3:1 while still maintaining a heat balance consistent with practice.) These conditions formed the starting point for all heat and mass balances in the upper reaction zones in the furnace.

Gases from the slagging zone rose into a 'furnace reaction zone' where the temperature of the downflowing charge was raised from 1000°C to the temperature of the slagging zone. The overall reaction rate was controlled by the rate of the carbon gasification reaction:

$$CO_2 + C \rightarrow 2CO \tag{5.3}$$

but otherwise, thermal and chemical equilibrium were maintained between the rising gas phase and the descending charge. Equation 5.3 is endothermic, counterbalanced by the exothermic reversions of reactions (Equations 5.1 and 5.2) to maintain the overall heat balance in the zone. A simplifying assumption again was that lead oxide had been reduced to metallic lead higher in the furnace. As a result of the carbon gasification reaction and because of the net outcome of the reversion reactions, the content of CO in the gas rose significantly. By using experimentally determined coke gasification rates and known mass balances for coke, slag and air rates, it was possible to calculate the time taken for the charge to rise from a nominated temperature to the 1150°C of the slagging zone temperature. An effective lower temperature limit of this zone of about 1000°C was consistent with residence time observations in practice.

In the 'top reaction zone', lead oxide was reduced exothermically – in the liquid state above 870°C and in the solid state below that temperature – by both zinc vapour and CO in the gas stream. Together with the physical heat transfer from the gases, the heat evolved by these reactions was absorbed in raising the temperature of the charge. The lower solids temperature limit for reaction in this zone was assumed to be 600°C, below which only heat transfer processes took place between gas and charge. A simplifying assumption used by Lumsden to solve the mass and heat balances in this zone was that the factor controlling the rate of chemical reduction processes was the rate of mass transfer of the reduction gases to the sinter surface; that is, resistance to the movement of PbO within the liquid or solid charge to the reaction interface was unrestricted. This allowed him to assume that the PbO activity at the reaction surface was unity and that the activities of CO(g) and Zn(g) were zero. The relative contributions of physical heat transfer and the heat of reaction to the overall heat balance in this zone could then be calculated by using a simple coefficient of fixed but unknown value assumed to relate the temperature and composition gradients in the gases. This calculation in turn allowed determining of the associated vertical temperature and composition gradients in the solids modified by the value of the unknown, but constant, coefficient.

Having set up his basic model established on the performance of the BHAS furnaces of the day, Lumsden then turned his attention to the implications of the reduction of the PbO content in the charge in a lead blast furnace being exothermic – a fact then not appreciated at Port Pirie. Surface reactions and their enthalpies were considered to be:

$$PbO(s) + CO(g) = CO_2(g) + Pb(l) \qquad \Delta H_{800} = -15.6\ \text{kcal} \tag{5.4}$$

$$PbO(l) + CO(g) = CO_2(g) + Pb(l) \qquad \Delta H_{1000} = -22.3 \text{ kcal} \tag{5.5}$$

$$PbO(s) + Zn(g) = ZnO(s) + Pb(l) \qquad \Delta H_{800} = -61.0 \text{ kcal} \tag{5.6}$$

$$PbO(l) + Zn(g) = ZnO(l) + Pb(l) \qquad \Delta H_{1000} = -67.1 \text{ kcal} \tag{5.7}$$

By varying the ratio of PbO to slag components in the charge, it was shown that at high ratios the solids temperature could rise above that of the gas temperature, leading to maxima in both the solids and gas temperature gradients. Under certain conditions – particularly where unreduced PbO persisted into the furnace reaction zone – the maximum solids temperature could be sufficiently high to allow partial fusion of the charge, followed by resolidification lower in the furnace. This provided a theoretical basis for the mechanism of charge softening leading to the bridging and hang-ups long observed in lead blast furnace operation at Port Pirie, but which had become a particular problem following the introduction of updraught sintering. The calculation was extended to estimate the maximum PbO/slag ratio, which could safely be tolerated for the CO_2/CO ratio prevailing in the slagging zone.

The Lumsden hypothesis provided an explanation for certain practical limitations in the performance of Port Pirie smelting practice, namely why:

- dilution of the exceptionally high-grade Broken Hill concentrates with recycled slag was necessary in the sintering operation in order not to exceed the tolerable percentage of oxidised forms of lead in the blast furnace feed
- the change from downdraught to updraught sintering, which resulted in a higher content of oxidised lead in sinter, initially caused problems in the blast furnace
- these problems were solved by partial reduction of the sinter with the addition of a small percentage of fine coke to the updraught sinter bed
- other potential modes of operation such as preheated air blast, steam injection, oxygen enrichment and so on were worth exploring.

The effects of varying CO_2/CO ratios in the equilibrium zone were also calculated. Excessive coke in the slagging-zone heat balance would lead to lower CO_2/CO ratios, higher volatilisation of zinc and PbS, upward extension of high-temperature reaction zones – even to the level of the stock line – and maintenance of the overall heat balance by the release of heat and CO to the exit gases that is characteristic of the well-known 'hot top' symptoms first noted by the early authors.

Although basic chemistry dictates that an energy and mass balance must apply to the furnace reaction column as a whole, the model provided a strong argument that the success of the blast furnace process depended on the setting up of a slagging zone sufficiently near the hearth, where the partial heat balance provided conditions of a particular oxygen pressure at a particular temperature to give an optimum department of lead into a bullion phase; that is, an equilibrium to yield the maximum achievable reduction of lead, and maximum achievable separation of slag and bullion. The compromise between these factors appeared to result in the consumption of excess coke reflected in the CO content of the exit gases. The model was then used to explore, by calculation, various options for operating a lead blast furnace that might result in lower coke consumption. These included the use of blast preheated to 400°C and the use of moist preheated blast. Somewhat surprisingly, these calculations did not include the possible use of oxygen-enriched blast, the advantages of which had already been demonstrated at other lead smelters (McNaughton *et al*, 1949). This possibility was later explored by other research department members at Port Pirie using calculation methods pioneered by Lumsden, but updated to include subsequently measured data. Later, when economical methods of generating small daily tonnages of industrial-grade oxygen had been developed that were suitable for use at an isolated site such as Port Pirie, plant trials confirmed the great benefit of what later became standard oxygen enrichment practice on the BHAS blast furnaces (Fern and Jones, 1980).

In summary, Lumsden proposed a thermochemical system based on different temperature zones, which required certain temperature and reduction potential conditions in the slagging zone of the furnace to satisfy the recovery and composition conditions of the discharge products. The associated circulation of volatilised reduction products and subsequent reoxidation higher in the furnace led to the production of excess energy above that required for charge heating and reduction processes. This excess energy was dissipated in the form of the sensible heat of the exit gases and chemical energy in the form of CO. Operating the lead blast furnace should then become a matter of meeting the physical and chemical requirements of the process while minimising the potential economic disadvantages of excessive coke consumption and restricted throughput because of premature fusion of the charge components.

That such objectives could be met by controlling the mass and energy balance of the furnace via the composition and feed rate of the sinter charge and manipulation of the associated rates of coke and blast air inputs is merely stating the obvious, since this had been operating practice for years. Yet this was a difficult industrial art in that there were no practical means for measuring either the hearth product parameters or the internal furnace conditions supposedly controlling them. The outcome of the operation depended on the subjective (but historically effective) assessment by the operator of several visual and operational clues and their relationship with furnace performance. Following internal publication of Lumsden's report, the question arose as to how real its several assumptions might be and whether its recommendations might be applied to practical blast furnace operation.

6

Reconciling Lumsden's Hypotheses with Practice

Despite the simplicity and elegance of Lumsden's assumptions in providing a theoretical explanation for most behavioural characteristics of lead blast furnaces – particularly those at Port Pirie – certain conceptual problems remained in reconciling the theory with field observations. For instance, the use of water-cooled jackets resulting in the formation of wall accretions clearly implied horizontal as well as vertical temperature gradients within the charge column. In any vertical plane through the tuyere axes, the double tuyere row configuration peculiar to Port Pirie meant that there were combustion zones at two tuyere horizons operating at different mass ratios of blast air, fuel and charge. There seemed little likelihood of such combustion zones combining to form the stable upward-moving horizontal temperature strata envisaged by the model. Observation at the charge stockline under normal operating conditions usually showed an irregular distribution of 'quiet' areas interspersed with hot zones with flame, often with the characteristic blue-white tinge indicating zinc vapour combustion, passing through red-hot charge. Moreover, such hot zones moved their location, disappeared and reappeared within quite short periods of time. Analysis of the exit gases at the stockline showed variation in the CO_2/CO ratio from 1:3 in the hot areas to 3:1 in cool areas. Experiments carried out in the early 1960s to establish whether stable temperature and gas composition gradients existed within the furnace column showed that both gas analyses and temperatures varied rapidly and unpredictably over the course of a few hours at any given sampling point on the cross-section of the furnace. These experiments were abandoned after only a few weeks' work, although later investigations showed that there was some value in using an overall furnace exit gas CO_2/CO ratio as measured in the offtake flue as an indicator of furnace conditions. The conclusion was, however, that direct sampling of gases over the cross-section and at depth in the furnace revealed no point that typified consistent reaction conditions at a given level.

This is quite understandable, given the background of extensive work carried out by the G K Williams research team during the 1930s to develop a suitable charging system for the very large BHAS furnaces (compared with other lead blast furnaces) (Green, 1977). The intention was to develop a system that would avoid excessive charge segregation by lump size and/or specific gravity – because of the marked differences between the physical properties of coke and sinter – yet result in a preferential passage of gases towards the centre of the furnace. The main gas discharge would therefore take place underneath the offtake hood. A furnace condition to be avoided was where the main discharge of gas from the charge tended towards the periphery, with the centre of the furnace cold and dead. Williams and his team eventually developed a double-rill system, where the charge from centrally mounted super-hoppers was controlled via hand-operated gates to pass downwards and outwards over the sloping offtake hood and towards the periphery of the furnace; once in the furnace, it would flow naturally back towards the centre, which was normally held at a lower level. While the intention was to produce a fairly uniform mix of coke and sinter with perhaps larger material towards the centre of the furnace, the unpredictable nature of the lead blast furnace process inevitably led to periodical ‘blows’; that is, a high velocity discharge of gas and fume at one point on the furnace cross-section, usually towards the periphery. Although the offtake volume capacity was several times that of the furnace gas produced, the localised velocity and volume of the gas stream from a blow was such that the majority of it escaped capture in the hood system, with obvious deleterious effect on the working and ambient environments. Thus, apart from the general design of the furnace feed system, several operating techniques were developed to anticipate and prevent the occurrence of blows:

- Careful furnace ‘trimming’ or adjustment of charge levels.
- ‘Barring’ to break up areas of potential charge fusion or for accretion removal to facilitate gas flow.
- Preferential feeding at potential breakthrough points.
- The use of lump slag (rather than sinter) or all-coke charges directed to a specific area of the furnace.
- A process known as ‘shaking’ – which is simply a disruption of the blast – so that the charge collapsed, particularly where blast channelling had caused large voids. It resulted in the burden reverting to a more uniform permeability; however, the overall permeability was also reduced and productivity suffered – it is hoped only in the short term.

It is obvious that the charge may have an uneven depth and that the horizontal distribution of coke and sinter tends to be anything but uniform with respect to mass and size. Furthermore, the various BHAS furnaces have operated with 80–92 tuyeres, arranged in up to four groupings within which all tuyeres were connected in parallel and between which blowing rates could be varied, such that the mass balance between sinter, coke and blast air could differ both horizontally and vertically in four separate areas of the furnace. Duties of the operating personnel included ‘punching’ of the tuyeres; that is, clearing the aperture of accretions formed as slag trickled into the region of the cold blast entry. The effort required for such an operation, carried out several times per shift, might vary from the manual insertion of a bar to the use of sledgehammers or even pneumatic hammers. Tuyeres frequently became bad or were lost, either through blockage by accretions or simply classified as such because there was no visible combustion zone. Since experience showed that over the course of time (sometimes days) and often as a result of remedial action in the charge above, the combustion zone in front of the tuyere could be re-established, the air supply to a ‘dead’ tuyere was seldom discontinued. Individual flows of air to the tuyeres were therefore far from uniform, but because of the complexity of the piping system, no systematic attempt was ever made to try to measure or control air flow distribution on an individual tuyere basis.

Lumsden’s concept presented an idealised picture of an evenly distributed gas stream of chemically and thermally uniform cross-section rising counter-currently to a similarly chemically and thermally uniform descending solid charge. The combined variabilities of coke/charge distribution and charge permeability, and the vagaries of a parallel supply of air via multiple tuyeres of varying diameter to combustion zones of varying activity and coke distribution render the achievement of this ideal highly improbable. The practical outcomes as demonstrated by variable temperature and gas analyses over the furnace cross-section were therefore only to be expected.

These findings do not necessarily invalidate the ideas inherent in Lumsden's model of the overall furnace. It would be perfectly valid to apply the same reasoning to each of a multiplicity of furnace elements reacting in a vertical direction according to the thermochemistry postulated by Lumsden. Such elements might relate to an individual tuyere or group of tuyeres operating within a range of quite different conditions, depending on the mass and energy balances of reagent materials arriving in a particular element. The products tapped from the furnace in a single stream would therefore represent an arithmetic average outcome of all reacting elements operating with a consistent input charge mix while still allowing for the variability of the upper shaft and the different behaviour of the two rows of tuyeres. Lumsden's model can therefore be taken to describe the behaviour of an average element reflecting that of the furnace as a whole. The real behaviour of any element may be quite different from the arithmetic average, since varying equilibrium relationships require that the product mass and energy distributions vary logarithmically with temperature. Following Lumsden's reasoning, such variation at the slagging zone level would result in differences in vertical dimensions and chemical outcomes of the upper zones of each element, finally becoming apparent as physical and chemical differences at the stockline.

This discussion is intended to show that the effects of crude but historically effective furnace operating practices on a highly complex and chemically sensitive reaction system could not be accounted for in terms of a consistent computer model combining thermochemistry with heat and mass transfer elements. There were simply too many uncontrolled factors involving random occurrences and subjective management decisions. It is therefore unlikely that Lumsden's concept could be used as a basis for process control of the Port Pirie blast furnace, or even as a model defining its day-to-day operations. Nevertheless, it must be remembered that Lumsden's first objective was to understand *why* the lead blast furnace behaves as it does, resulting in what appears to be an excessively high fuel consumption. It is only in the latter part of his paper that he attempted to use his model predictively, and this must be questioned in light of experimental evidence. If, however, Lumsden's chemistry is applicable with variations to each of a multiplicity of furnace reaction elements, then it is still worthwhile to continue examining his assumptions.

Slagging zone equilibrium

The existence of a region towards the hearth in which gas, slag and metal are in equilibrium is fundamental to the Lumsden (1971, 1960) models of both the ISF zinc/lead blast furnace and the lead blast furnace. In each case, a fixed point of reference is established that is consistent with mass and energy balance data observed in practice. With certain assumptions, his models then allow a mathematical description of the sequence of reactions and heat and mass transfer in the preceding zones higher in the furnace. The question arises as to whether the equilibrium concept models the reality or is merely a mathematical convenience. A modification, already suggested, is that in allowing for variations in observed behaviour over the area of a lead blast furnace, such a model can also apply to individual elements. Each would have differing reaction conditions within the same chemical system as determined by mass and energy balance conditions in the region of single – or groups of – tuyeres.

The idea that high-temperature metallurgical reactions can take place under conditions closely approximating those of chemical equilibrium has long been a traditional belief in the smelting industry. This was manifested in the early 20th century technical literature by the widespread use of phase diagrams to illustrate metallurgical phenomena. After World War II, the limitation of two-dimensional diagrams gradually gave way to the use of more sophisticated thermodynamic descriptions of the behaviour of the complex multi-element phase systems involved in metallurgical processes, but the idea of an equilibrium constraint on reaction outcomes remained. At lower temperatures, it was accepted that although equilibrium thermodynamics might determine the direction of chemical change, the outcome was limited by reaction kinetics. Somewhere in between these two modes of chemical control, there could be a region in which the products from a rate-limiting kinetically controlled reaction stage could achieve a state of equilibrium with other reagents. Such an approach is explicit in Lumsden's considerations in his furnace reaction zone and implicit in the state-of-the-art review of the then-current physical chemistry of lead smelting by Willis (1980), where much of the outcome of lead blast furnace smelting was discussed in equilibrium terms. As traditional processes began to give way to more intense new processes such as flash smelting of sulfidic concentrates and injection of solid reagents and gases into molten baths, it became apparent that reaction kinetics could also determine the outcome of high-temperature metallurgical reactions. Essentially kinetic models of the operation of lead blast furnaces were produced by Madelin, Sanchez and Rist (1990) for Metaleurop at Noyelles-Godault, and Zhao (1993) for BHAS/Pasminco at Port Pirie. Russian-language papers describing experiments at Chimkent[2] in Kazakhstan, as collated by Polyvyannyi (1976), considered only the kinetics of lead blast furnace chemistry as applied to pilot and full-scale operations, but without producing a mathematical model.

Hollitt (1992) discussed the claims of the protagonists of the equilibrium/kinetics debate and concluded that, within limitations, both sides could be right. Global equilibrium requires the rate of mass transfer to be so high and concentration gradients so small that the reacting system achieves instantaneous equilibrium at all interfaces. Local equilibrium, as the more likely case, allows that the actual interface between phases at high temperature can be at equilibrium, but that the supply of reactant species to the interface can be limited by mass transfer and hence by concentration gradients on one or both sides of the interface. Lumsden (1960) took such points into consideration while arguing the case in favour of what is essentially a global equilibrium in the slagging zone and local equilibrium in the furnace reaction zone.

An equilibrium outcome requires that, in accordance with the general reaction:

$$\mathrm{Me(metal)} + \tfrac{1}{2}\mathrm{O}_2 = \mathrm{MeO(slag)} \tag{6.1}$$

the equilibrium constant is:

$$K_{6.1} = \frac{a_{\mathrm{MeO(slag)}}}{a_{\mathrm{Me(met)}} * p_{\mathrm{O}_2}^{1/2}} \tag{6.2}$$

Thus, under equilibrium conditions at a given temperature, the oxygen pressure can be calculated from the known equilibrium constant and the partition of reducible species between slag and metal phases. Further, the oxygen pressure should vary as the square of the partition ratio. In the lead blast furnace this should apply to both zinc and lead and, by extension, to similar relationships for ferric/ferrous iron species.

Lumsden (1960) used the partition of zinc to estimate the oxygen pressure in his slagging zone in the Port Pirie furnaces. He concluded that chemical analyses for zinc in product slag and bullion showed that equilibrium would have been attained with a CO_2/CO ratio of 4:1 at about 1150°C. Since that time, there have been many more investigations evaluating the activity of zinc oxide in molten slags that allow an improved estimate of its activity

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[2] As of 1993, Chimkent is known as Shymkent, but as these examples occurred before the name change, all references will be to the former name.

coefficient from the slag composition. For the solid ZnO reference state, a_{ZnO} for a typical Port Pirie slag can now be estimated at 0.58 at 1200°C and 0.67 at 1150°C, compared with Lumsden's values of 0.74 and 0.82. For a range of zinc content in Port Pirie bullion from 0.05–0.07 per cent, the newer values yield estimates of $\log_{10}p_{O_2}$ from -9.74 to -10.02 at 1200°C and -10.56 to -10.86 at 1150°C. These may be compared with $\log_{10}p_{O_2}$ of a typical Port Pirie slag measured in the laboratory by Hollitt (1984a) as -10.01 at 1200°C and extrapolated to -10.65 at 1150°C. A further comparison of interest is with the $\log_{10}p_{O_2}$ values directly measured by Fontainas, Verhulst and Bruwier (1985) on 250 production lead slags from the lead blast furnace at Hoboken, Belgium. For slags of similar CaO/SiO_2 ratio to the Port Pirie slag, $\log_{10}p_{O_2}$ values at 1150°C and 1200°C, and 2.5 per cent residual lead in slag can be calculated by interpolation from their statistically determined relationship to be -10.58 and -9.72 respectively. These measured $\log_{10}p_{O_2}$ values are consistent with those calculated from the zinc partition, and also suggest an equilibrium CO_2/CO ratio of 3:1 rather than the 4:1 estimated by Lumsden.

Evidence from lead partition under industrial conditions is questionable because of the practical difficulty of determining the concentration of oxidised lead in slag within the total lead content reported by the usual assaying methods. Willis (1980) mentioned several laboratory investigations showing oxygen partial pressures that varied with the square of the lead concentration in slag in agreement with Equation 6.2; however, estimates of the activity coefficient γ_{PbO} calculated from oxygen partial pressures and lead concentrations derived from industrial practice showed wide variation. Willis ascribed this to uncertainty in the techniques used, which varied from estimates from zinc and lead partition between slag and bullion, to measures of the Fe^{3+}/Fe^{2+} ratio in slag or analyses of tuyere gases. At the time, none of these could be considered rigorous for theoretical or practical reasons. The anomalies led to a BHAS-sponsored project in which oxygen potentials on both synthetic and industrial slags were directly measured by Hollitt (1984a, 1984b). His conclusion, based on a methodology that included careful electron microscopy of the phases in a quenched sample of Port Pirie production slag, was that lead oxide comprised only about 0.52 per cent of the slag mass compared with a total lead content of 2.3 per cent in the original sample. The experimental technique was carefully controlled so as to preclude significant reaction of the sample during the seven-hour equilibration time, leading to the conclusion that the true value of γ_{PbO} was four to five times greater than that generally accepted at Port Pirie at the time as a result of estimates by Lumsden (1960) and Grant (1980).

Lumsden (1960) attempted to show that the concentration of lead in Port Pirie slag was consistent with the oxygen partial pressure measured by the zinc partition. A confirmatory value of the oxygen partial pressure was derived by adopting the then prevailing paradigm at Port Pirie that the assay for total lead in slag was a measure of its PbO content. Justification for this tenet can be traced to speculation arising from observation by Manson and Segnit (1956) of lead blebs rimmed by magnetite crystals in the Port Pirie slag. While lead prills had been observed in microscope studies, any metallic lead in the slag could be considered to have been formed by the reduction of PbO by FeO during cooling. Additional evidence for this claim seems to have been that the silver content of the slag was so low as to be negligible compared to what would be expected if the prills consisted of entrained bullion. Accordingly, by using the value of $\gamma_{PbO} = 1$ estimated by Richardson and Pillay (1957) and the average total lead in slag prevailing with the then current design of the blast furnace hearth arrangement (about 1.5–1.8 per cent), Lumsden arrived at an apparent consistency with the oxygen partial pressure calculated from the zinc partition.

In this matter Lumsden was in conflict with the findings of several prior BHAS-sponsored studies summarised by Manson and Segnit (1956), as well as that of Richardson and Pillay (1957), which showed that the proportion of metallic lead in granulated (that is, shock-chilled) slag could amount to 30–70 per cent of the total lead in slag. Reconstruction of the Port Pirie blast furnace in 1964 with a new hearth and slag tapping configuration brought about a step-change increase in slag lead content from 1.5–2.0 per cent to 2.5–3.0 per cent without affecting the zinc partition chemistry. Operational staff ascribed this to the reduced slag settling time resulting from the structural changes. Moreover, later statistical studies showed a variation of slag lead content with slag throughput rate (for example, Barnett, 1976). Thus, both laboratory and practical evidence suggested that the phase separation of bullion and slag had always been incomplete in Port Pirie blast furnace operation.

In the study by Grant (1980), ZnO and PbO activity coefficients were derived from operational parameters at the BHAS slag fuming plant on the assumption that the metallic lead content of the slag was volatilised early in the batch fuming cycle, so that for the slags under consideration, lead was present only in an oxidised form. A consistent value for γ_{ZnO} at 1200°C was derived for the observed range of ZnO concentration during slag-fuming batch cycles. The relationship between a_{PbO} and the supposed value of the mol fraction N_{PbO} (calculated from the total lead in slag assay) was anomalous in that γ_{PbO} varied widely over the concentration range. In retrospect, this can be ascribed to the probable presence of metallic lead that had been assumed to be absent in the investigation. Similar difficulties in determining consistent values for γ_{PbO} were experienced by Wright, Denholm and Rankin (1989), who used lead blast furnace slags in laboratory studies to determine γ_{ZnO} and γ_{PbO}. The equilibrium behaviour of zinc was consistent with the requirements of Equation 6.2, while that of γ_{PbO} as a function of the presumed value of N_{PbO} was erratic.

Advances in analytical techniques now allow accurate determination of the residual silver content of blast furnace slag. A simple calculation now agrees with both the Hollitt and the earlier microscopic estimates of entrained bullion in Port Pirie slags. Lumsden's contention that the residual concentration of lead in slag supported the estimate of the oxygen partial pressure derived from zinc partition was therefore in error.

For practice at a particular operation, it would be expected from Equation 6.2 that for a given temperature under equilibrium conditions, p_{O_2} should vary as the square of the PbO activity in the slag, assuming that the activity of lead in bullion should consistently remain at or near unity. Fontainas, Verhulst and Bruwier (1985) investigated whether, as a possible method of process control, direct oxygen potential measurement using commercially available probes could be related to the lead content of slags in contact with lead bullion. For processes under development and for the lead blast furnace, the lead level of a particular slag composition at a particular temperature could be predicted from an oxygen potential measurement to an accuracy of ±10 per cent relative error. Their statistical relationship for lead blast furnace operation was:

$$\log_{10}(p_{\mathrm{O}_2}) = -27\,160/T + 1.46\log_{10}(\%\mathrm{Pb}) + 7.92 \tag{6.3}$$

over the temperature range 1100–1180°C and per cent Pb in slag 1.0–2.5 per cent. Variation of $\mathrm{CaO/SiO_2}$ between 0.45 and 0.8 did not significantly alter the correlation. The coefficient for the log (per cent Pb) term is below the equilibrium value of 2. An equilibrium relationship also requires that there should be no numerical constant. The authors, however, expressed reservations about the use of per cent Pb as a surrogate for the residual PbO activity because of entrapment of metallic lead in the slag. Their measured oxygen pressure values were consistent with other values determined from industrial slags as tabulated by Willis (1980) and Hollitt (1984a), and also with those determined in the laboratory under controlled equilibrium conditions by Wright, Denholm and Rankin (1989).

The experimental evidence thus shows that unless both the entrained metallic lead and the lead oxide contents of a lead blast furnace slag can be accurately determined (as in Hollitt's study), the total lead content of slag as determined by traditional assay methods cannot be used other than as a site-specific indicative measure of its oxygen partial pressure. The sum of the metal and oxide represented by the total lead assay therefore cannot be used as an accurate determinant of thermodynamic performance of the reduction reaction, and certainly not as proof or otherwise of equilibrium conditions within the blast furnace.

In theory, equilibrium between ferrous and ferric iron species should also determine the oxygen potential of the slag. The analysis of ferrous iron in lead blast furnace slag by the wet chemical method used at Port Pirie during the 1970s (that is, by decomposition in an inert atmosphere followed by titration with an oxidising solution), was rendered invalid by the presence of oxidisable species such as sulfides and the indeterminate proportion of metallic lead. A ferrous/ferric ratio for Port Pirie blast furnace slag was sometimes cited in early reports (for example, Richardson and Pillay, 1957), but the resulting estimate of the blast furnace oxygen partial pressure differed considerably from that calculated by Lumsden (1960) from zinc partition. Accordingly, the analytical method fell into disuse for some years until a modified technique was adopted to determine the ferrous/ferric ratio in partially dezinced slag-fuming process slags. In this case, the influence of metallic lead and sulfides on the assay method was assumed to be negligible (Grant, 1980).

In summary, the only strong evidence for an equilibrium-controlled outcome for the products of reaction in the slagging zone of the Port Pirie lead blast furnace comes from zinc partition data supported by zonal heat balances influenced by the associated volatilisation effects. While the lead content of production slags varies with oxygen pressure – as would be expected for equilibrium control – the practical difficulty of accounting for the proportion of metallic lead entrained in the slag only allows support for, rather than proof of, an equilibrium outcome.

Later, it will be shown in this volume that assuming a hearth zone equilibrium also satisfactorily explains the deportment of sulfur in the gas-slag-bullion phase system; this is particularly in relation to long-standing operational problems of formation of different types of ZnS-rich accretions in different locations in the hearth area.

It is interesting to compare the concepts put forward by Lumsden (1960, 1971) with the findings of Madelin, Sanchez and Rist (1990), who reported on investigations on both ISF and lead blast furnaces at Metaleurop's Noyelles Godault operation. For the ISF, these authors were able to identify an equilibrium point at 1015°C and, using a more modern approach to reaction kinetic mechanisms in the upper furnace, developed a heat and mass transfer model that adequately simulated practice. The methodology of heat balance calculations for the lower furnace zone of the ISF was not described, but the context suggests an approach similar to that by Lumsden for the Port Pirie lead furnace. For the lead blast furnace investigations, however, the limited number of vertical temperature/gas analysis probes did not identify any 'thermal reserve' zone indicative of an equilibrium zone. A consequent conclusion was that no equilibrium point existed in the lead blast furnace, requiring a kinetic approach to modelling of its chemistry. For his lead blast furnace model, Lumsden (1960) showed that according to the mass and energy balances resulting from both the higher CO_2/CO ratio and zinc content in the slag, equilibrium would be achieved at a temperature of about 1150°C and, further, that the equilibrium zinc content and temperature of the slag were essentially those of the slag as tapped. This indicated that, unlike the ISF, the equilibrium and slagging zones would be coincident. Given this conclusion, it is not surprising that no confirmation of equilibrium could be found from gas temperature and composition profiles in higher zones in the furnace. A notable and surprising omission in the study by Madelin, Sanchez and Rist (1990) is that no account seems to have been taken of the role of zinc volatilisation processes in lead blast furnace smelting, despite their investigations showing that an equilibrium involving the same volatilisation chemistry existed at a lower temperature within the ISF. Lumsden's study considers the profound effect of such volatilisation in limiting the temperatures achieved in the tuyere zone, as well as on the mechanism of heat transfer via a combination of mass transfer and reaction of gaseous species at the charge interfaces, with consequent effect on the temperature profiles of gas and charge components higher in the shaft. A similar lack of appreciation of the volatilisation chemistry is noted in the study by Zhao (1993) based on the Port Pirie furnace. Insofar as the activity of ZnO in the Port Pirie slag is unusually high (and deliberately maintained so), it may be argued that zinc volatilisation plays a greater role than in the Noyelles Godault lead furnace. No composition of the slag was given in the study by Madelin, Sanchez and Rist (1990), but the generality of lead smelting practice is that the zinc content of the slag is always significant, and the highly endothermic effect of its reaction at the temperatures and oxygen pressures of the lead furnace should not have been ignored.

It must be acknowledged that the Lumsden technique – in which averaged eight-hour operating data are used to represent heat and mass balance conditions controlling the compositions and outlet temperatures – may only approximately describe average medium-term conditions that vary strongly in the short term and spatially over the length of the furnace. A legitimate criticism would be that local variations in temperature and mass balance should be reflected in logarithmic – rather than arithmetic – changes in equilibrium distributions depending on thermodynamic relationships; however, operating experience shows that successful blast furnace smelting in terms of consistency of throughput, fuel efficiency, product bullion and slag compositions is entirely achievable through control of the overall input mass balance – blast air, sinter, coke and minor quantities of ancillary materials such as refinery and other lead-bearing recycles. In the longer term – towards the end of an operating campaign when throughput declines because of furnace profile changes resulting from accretion formation deep in the furnace column – output composition parameters can still be maintained despite changes in the overall energy balance. This suggests that the key control parameters under conditions of fluctuating throughput are product temperature and oxygen partial pressure; that is, factors dependent on maintaining appropriate chemical equilibrium conditions. Despite neither of these properties being able to be conveniently and continuously measured by instrumental methods in the field, it must be acknowledged that blast furnace personnel develop extraordinary skills in maintaining satisfactory operations by observing related properties of slag colour and fluidity together with acceptable top conditions.

An influence of kinetics?

An investigation of possible relevance to the discussion of an equilibrium in the slagging zone chemistry is that of Polyvyannyi *et al* (1971), who investigated the course of reactions in a pilot-scale lead blast furnace by replacing the blast with nitrogen to freeze the furnace, and then sectioning and analysing the burden. These authors clearly viewed lead reduction reactions in the hearth zone – occurring downwards from a level of about 700 mm above the tuyere axis to what they termed the 'bath level' – as a continuation of kinetically controlled reactions higher in the furnace. At a gas temperature of 1200°C at the 700 mm level above the tuyere axes, reduction was about 70 per cent complete, rising to 85–90 per cent completion at the tuyere zone. The remaining unreduced species were silicates and sulfides.

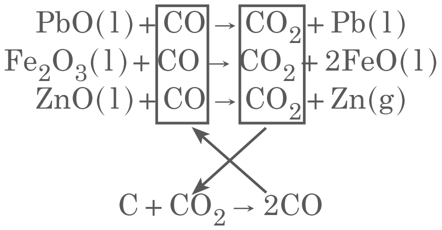
That significant amounts of unreduced lead remained in the descending charge in the temperature range where slag formation took place might cast some doubts on the Lumsden model in respect to slagging zone behaviour in the Port Pirie furnace. His heat balance in this zone requires the assumption that lead reduction is completed in the kinetically controlled upper zones of the furnace, allowing equilibrium conditions to be achieved in the slagging zone. The question is whether the pilot-scale experiments at Chimkent can be an adequate general representation of lead blast furnace behaviour that can be extrapolated to Port Pirie practice. A comparison of specific production rates shows that the small Chimkent experimental furnace produced at a rate 2.5 times greater than that of the Port Pirie furnace (50 t/m^2.day compared with 20 t/m^2.day). With comparable burden heights and sinter compositions in each case, this roughly translates to a residence time of the reduction mass in the Port Pirie furnace being 2.5 times greater than that in the Chimkent experiment. This considerable difference suggests that the Lumsden assumption is not necessarily invalidated by the Chimkent work.

Polyvyannyi *et al* (1971) state that the reduction of residual slow-reacting silicates was completed in the tuyere zone. On the other hand, their phase analysis tables (which included material taken from *below* the tuyeres) suggest that further reduction of lead classified as silicate took place in this region via direct reaction with coke. At the tapping level, the slag layer contained about 1.6 per cent lead characterised as silicate compared with 4–5 per cent at the tuyere zone. That such further reduction of the lead content of the fully formed molten slag can take place in a lead blast furnace should not be surprising. The solid materials in the subtuyere zone that support the entire mass of the furnace burden must consist mainly of residual coke, since temperatures here must be well above the slag liquidus in order for slag to freely drain towards the taphole. All reaction products from higher in the furnace must therefore flow as liquids through a carbon-rich zone at high temperature. From their physical and chemical examinations of the frozen furnace burden, the authors believed that the major kinetically controlled reaction for the reduction of silicates in the tuyere zone was via direct contact between molten silicates and solid carbon. This conclusion was based on prior laboratory studies of reduction mechanisms, which had shown that reduction of molten silicate glasses by solid carbon was much faster than by gaseous CO (Polyvyannyi, Vasilieva and Ivakina, 1971). Later experiments described by Polyvyannyi (1976) showed that the rates of reduction of sinter in the temperature range 800–1200°C by powdered carbon were no faster than by gaseous carbon monoxide. Both sets of experiments had shown that the migration of PbO from within the liquid phase to the phase boundary was not a limiting factor; this resulted in kinetics close to first order during the initial stages of reaction, but later slowing as the interfacial surfaces became occluded with reaction products. It is logical that similar mechanisms apply to the reduction of molten slag in contact with carbon, and it is well demonstrated in the coke bed of the Kivcet process by the intensive reduction of the molten oxidic lead product from the oxygen flash smelting of lead concentrates.

In the Kivcet process, a charge consisting of lead concentrates, recycles, fluxes and carefully sized carbon reductant is burned by industrial-grade oxygen in a flash smelting chamber. The concentrates are substantially oxidised in the combustion flame to form an oxide melt and off-gas of high SO_2 content. The carbon is ignited and partially burned, then gravitates with the fluxes and molten products to the base of the combustion chamber, forming a high-temperature carbon reduction bed through which the oxidised products trickle; these coalesce to form a melt that flows over the carbon in a thin film, which is reduced to metallic lead and a low residual lead slag. The reduction process is extremely fast, taking place to virtual completion in a carbon bed only ~200 mm in depth. Research at VNIItsvetmet, Ust' Kamenogorsk, Kazakhstan on the chemistry that allowed the design modelling of the industrial-scale process has been collated by Lyamina and Shumskii (2003). There are physical and chemical similarities between this zone of the Kivcet furnace and the subtuyere zone of the lead blast furnace.

The conclusions from the VNIItsvetmet reduction investigations can be summarised:

- The molten oxide phase is not directly reduced by carbon. Reduction takes place by a cyclic process through a thin film of gas phase consisting of a mixture of zinc vapour and CO and CO_2 between the carbon and molten phases. It involves parallel stages of reduction of the oxide melt by carbon monoxide and oxidation of carbon by its dioxide.
- Studying the kinetics of the possible reactions under the coke bed conditions allows the effective reactions in the system to be simplified to the heterogeneous reactions in the temperature range 1250°C–1400°C:



$$\left.\begin{array}{ll} PbO(l)+\boxed{CO}\rightarrow\boxed{CO_2}+Pb(l) & -97\text{ kJ/mol} \\ Fe_2O_3(l)+\boxed{CO}\rightarrow\boxed{CO_2}+2FeO(l) & +45\text{ kJ/mol} \\ ZnO(l)+\boxed{CO}\rightarrow\boxed{CO_2}+Zn(g) & +130\text{ kJ/mol} \end{array}\right\}\text{Oxide melt} \qquad (6.4a–c)$$

$$C + CO_2 \rightarrow 2CO \qquad +164\text{ kJ/mol} \quad \text{Reductant} \qquad (6.5)$$

  Rates of homogeneous reactions, volatilisation of lead compounds and diffusion processes were not significant in modelling the kinetic behaviour of liquid-phasereduction in the bed. ZnO reduction, although slow relative to that of Fe_2O_3 and PbO, was nevertheless significant because of the circulation of zinc in the bed arising from volatilisation in lower zones and re-oxidation of zinc vapour in the upper parts of the bed.
- The overall endothermic outcome of this reaction sequence starting with separate solid particles and molten droplets containing lead oxide, fluxes and carbon is such as to require an external heat input to the bed to prevent bed temperatures from falling below the slag liquidus temperature; that is, 'freezing of the bed' (Lyamina and Shumskii, 2003). In the Kivcet process, additional heat is provided to the base of the reduction bed via circulation of slag at an elevated temperature in the common hearth between the flash smelting/reduction chamber and the connected electric settling furnace. The heat flow from this source is inversely proportional to the bed depth, such that the bed depth becomes an important operating variable in maintaining thermally stable operating conditions.
- By making the assumption that the carbon and melt surfaces have the same surface areas and temperatures, and by using physical and chemical reaction parameters determined from pilot-scale and laboratory investigations, a mathematical model was developed describing the thermochemical behaviour of the reduction bed in the Kivcet process. This model has been used to evaluate the effects of the reactivities of different carbon reductants and lead-bearing raw materials in the coke bed, as well as to analyse and optimise the operation of processes in industrial-scale Kivcet units.

The account by Lyamina and Shumskii (2003) suggests an emphasis on understanding the relationship between the chemistry and thermal effects during the initial intensive reduction stages in the upper 10–20 per cent of the coke bed; this is particularly in relation to the undesirable crystallisation of unspecified high-melting phases. The review gives no details of the experimental methods used to determine the kinetic parameters for the individual reduction reactions, which allowed the identification of the rate-controlling reactions as outlined. There is considerable discussion about investigations into the kinetics of the reaction in Equation 6.5 in respect of the potential use of reductant carbons other than metallurgical coke. The effect of varying the temperature of the underlying molten slag layer on bed temperatures to offset thermal deficiency in the reaction bed is demonstrated by the model results. There is no discussion of the modelling results relating to the final stages of lead reduction in the lower parts of the bed. Thermal effects are outweighed by heat input from the underlying higher temperature slag layer. Typical modelling results of the variation of reducible slag component concentrations with bed depth show that lead contents are reduced to <2 per cent and below in the lower 50 per cent of the bed, while Fe_2O_3 continues to be reduced slowly over the whole depth.

In a related study pertaining to the Kivcet process as operated at Teck-Cominco's Trail (Canada) operation, Kinaev, Jak and Hayes (2005) also considered the kinetics of reduction of lead smelting slags by solid carbon. In their experiments, the rates of reduction of PbO and Fe_2O_3 in zinc-free synthetic slags were examined at various temperatures and concentrations at various SiO_2/CaO ratios. The PbO concentration was varied between three and 100 per cent. A carbon rod (graphite or metallurgical coke) of fixed geometry was completely immersed in a small crucible of fully molten slag and rates of reduction measured via the volume and composition of the exit gases. Their results confirm that reduction was via a cyclic process set up in the gas film between the carbon surface and the molten slag. Overall, first order reaction rates (that is, the rate of removal of reducible oxygen deriving from the reduction of PbO and Fe_2O_3) were largely independent of SiO_2/CaO and SiO_2/Fe ratios. Rates were also independent of carbon type, indicating that the gasification reaction in Equation 6.5 was not the rate-controlling step and the rate of CO production at the carbon surface was fast compared with other reaction steps. Accordingly, the partial pressure of CO in the gas film must have been close to the equilibrium value of one at the carbon surface. Examination of the slags after quenching showed no liquid-phase concentration gradients to suggest slag phase mass transfer as rate-controlling. Other studies indicated that gas phase mass transfer was not limiting. Product gas analyses in all tests, however, showed high CO_2 concentrations closely approaching equilibrium with the slag phase. The authors suggest that the apparent conflict between the exit gas analyses and the p_{CO} value of one in the gas film indicated by the reaction kinetics is explainable by the experimental geometry, whereby exit gas bubbles escaping the system could not return to react with the carbon surface but were free to react with the bulk slag. It was concluded that the rate-limiting step in the reduction of $PbO–FeO–Fe_2O_3–CaO–SiO_2$ slags by solid carbon is the chemical rate of removal of oxygen at the gas/slag interface, empirically expressed as:

$$r_O = k_O^{app}(CO_2/CO)(slag)[p_{CO}](g) \qquad (mol\ O\ m^{-2}s^{-1}) \qquad (6.6)$$

where:

r_O	is the rate of removal of reducible oxygen (associated with ferric and lead oxides) from the slag
k_O^{app}	is the experimentally determined rate constant
$(CO_2/CO)(slag)$	is a measure of the oxygen activity in the slag via the equilibrium $CO(g) + O(slag) \rightleftharpoons CO_2(g)$
$[p_{CO}]$	is the partial pressure of CO in the reduction gas

Equation 6.6 implies that the reduction process should generally apply to zinc-bearing slags also and, by extension, to those in the subtuyere region of lead blast furnaces. Vertical concentration gradients in respect of the lead oxide and ferric oxide contents of the slag and temperature should therefore exist between tuyere and slag tapping levels in this region of the furnace. The change in average lead concentration in the charge between tuyere and tapping levels observed in the Chimkent pilot furnace trials (Polyvyannyi *et al*, 1971) is qualitatively consistent with such a reaction system, but as previously discussed, operating conditions were not comparable with those in the large-scale Port Pirie operation. Nevertheless, despite the very real differences relating to bed geometry, boundary conditions, flow patterns and temperatures between the subtuyere zone of the lead blast furnace and the Kivcet process coke bed, it is reasonable to consider whether the chemistry of reduction of substantially reduced molten blast furnace slag by 'direct' contact with coke is significant in the overall mechanism of reduction in the Port Pirie furnace.

Lyamina and Shumskii (2003) make it very clear that their model is specific to the conditions set up in the Kivcet coke bed and much simplified from the overall general scheme for reduction in the PbO-ZnO-FeO-CaO-SiO_2 system. The most significant factor in their case is the ratio of the surface area of the carboniferous reductant to the volume of oxide melt, which determines the contribution of heterogeneous and homogeneous reactions as well as diffusion mechanisms to the overall process. In the Kivcet scheme, assuming that the melt is in the form either of small droplets or a thin film dispersed over the coke bed, the surface area to volume ratio is estimated at $\sim 10^5$ m^{-1}. Further, the liquid film thickness in this case is of the same order as that of the gas layer separating the melt and carbon surfaces. The effects of both gas and liquid-phase diffusion could therefore be discounted in the kinetic model of Kivcet coke bed reduction.

In the blast furnace, the descending slag is already fully formed at the tuyere zone level and, according to the Lumsden model, in equilibrium with separate descending bullion and rising gas phases. Should further reaction with residual coke take place as the slag flows downwards through the subtuyere zone, it follows that the final slag, as tapped, should be at a lower oxygen potential than the tuyere zone equilibrium. A further consideration in the case of the Port Pirie hearth configuration is that slag from the remote ends of the furnace must flow an even greater horizontal distance than the vertical subtuyere height as it moves towards the tapping point through a solids layer, which, in the case of an operating furnace as contrasted with the Chimkent short-term pilot furnace, consists of residual coke and sulfidic accretions. Supporting evidence for the concept of kinetically controlled reduction in the subtuyere zone may be provided by the experience of the step change in the lead content of exit slag (from 1.5–2.0 per cent to 2.5–3.0 per cent) following the introduction of the new furnace design at Port Pirie in 1964. The new furnace had a smaller depth from tuyere to tapping level; the maximum horizontal slag flow distance from furnace end to tapping point was 30 per cent less while the specific production rate (tonnes product per m^2.day) was about 30 per cent greater. All these factors would have provided a significant diminution in contact time for kinetically controlled reduction compared with the older furnace design. The same factors, however, also reduce the time available for the phase separation of slag and metallic lead droplets, which comprise the much larger fraction of the total lead content. Because the oxidised and metallic constituents of the slag were not separately accounted for in Port Pirie operations, industrial experience cannot therefore provide conclusive evidence as to further kinetically controlled reduction in the subtuyere zone. Compared with the small droplet/thin film concept of slag flow in the Kivcet coke bed, the mechanism of molten slag formation in the lead blast furnace is by reduction and melting of lump sinter charge to form the coherent streams observable through the tuyere eyehole glasses. It is therefore likely that the reaction surface to volume ratio in the subtuyere zone of the blast furnace is considerably less than in the Kivcet coke bed, with consequent effect on the rate of oxygen removal from the slag by direct reduction.

A further consideration is that of occlusion of the surface of the carbon by metallic lead noted by Kinaev, Jak and Hayes (2005) as the reason for deviation from first-order kinetics after the first few minutes in their reduction experiments. For this reason, a diminution in the availability of the carbon surface in the subtuyere zone under lead blast furnace conditions is likely to be real but undefinable.

Under equilibrium conditions in the tuyere zone, the mole fraction of Fe_2O_3 is roughly 30 times that of the PbO in the slag. Thus the great majority of the oxygen molecules removed from the slag by carbon reduction in accordance with Equation 6.6 must be supplied by the reduction of Fe_2O_3, an inherently slow reaction compared with that of PbO (the absolute reaction rate constant for PbO is about eight times that of Fe_2O_3; Lyamina and Shumskii, 2003). Under the conditions of the Kivcet coke bed, modelled composition curves at 1300°C show a continuing slow diminution of the Fe_2O_3 content of the slag in the lower half of the bed while the change in PbO is almost undetectable. By extension to blast furnace conditions, the same effect in respect of Fe_2O_3 should occur, but to an undefinable extent. No change would be noticeable in the total lead content because of the predominating effect of entrained metallic lead.

In summary, it would be expected that there should be some decrease in the oxygen partial pressure of the slag in the lead blast furnace as it passes through the subtuyere zone. The effect is not definable. The inclusion of the subtuyere zone as part of an overall equilibrium in the slagging zone would seem not unreasonable, because any effect is small compared with other variabilities associated with the use of averaged industrial data in the calculation of slagging zone mass and energy balances.

Reduction in the furnace shaft

Inherent in the concept of slagging zone equilibrium is that the exit gases rising from the zone at a temperature of 1150°C are in equilibrium with slag containing zinc oxide at a significantly high activity. Accordingly, the gas phase zinc vapour pressure is also significant. This is the concept on which the successful operation of the ISF zinc blast furnace and the slag fuming process depends. For an equilibrium gas in which the CO_2/CO ratio is 3:1, and following Lumsden's method of calculating mass and energy relationships on a per mole carbon burned in the tuyere zone of the Port Pirie lead blast furnace, the equilibrium molar ratios for $CO_2/CO/Zn$ in the gas are calculated to be 0.75/0.25/0.27. The magnitude of the molar concentration of zinc in the gas is therefore of the same order as that of CO at the reference temperature at which the modelling of reactions in the upper part of the furnace must commence. Thus, not only does the reversion of zinc vapour to ZnO by reaction with CO_2 as the gas cools have a significant effect on heat distribution between gas and charge phases, it also has an effect on the CO_2/CO ratio. Furthermore, zinc vapour at high temperatures is a significant reductant with respect to reducible oxides such as PbO and Fe_2O_3 in the charge. This is a point, referred to by Willis (1980) and Blaskett and Boxall (1990), which was well understood at Port Pirie but not by several later modelling studies (Madelin, Sanchez and Rist, 1990; Hussain and Morris, 1986; Zhao, 1993). Zinc volatilisation was noted in pilot blast furnace trials at Chimkent in Kazakhstan (Polyvyannyi, 1976, and also in calculations by Chao *et al*, 1978), but not accorded any significance.

For the purpose of this discussion, reduction in the furnace shaft consists of those reactions taking place in the lead blast furnace between the charging level, at which the incoming solids are effectively at ambient temperature, and those regions of the furnace where reduction has been substantially completed and the rising gas and descending reduced charge are essentially at chemical and thermal equilibrium at a temperature of 1150–1200°C. This rationalisation is necessary because the complexity of the double tuyere configuration of the Port Pirie furnace makes it impossible to define geometrically a characteristic temperature distribution at any particular horizon in the shaft. The commonality between the Port Pirie furnace and those at other operations is that vertical temperature gradients in the burden must exist in all cases, and are necessarily determined both by the thermochemistry of reaction between the rising gases and the coke and descending metal oxides in the sinter, as well as by heat transfer mechanisms.

In the Lumsden models of the zinc/lead and lead blast furnaces, the equilibrium zone within the furnace burden provides the fixed reference point, determined by energy and mass balances from practice and fundamental thermochemistry, from which gas, liquid and solid phase compositions and temperatures can be estimated. In the lead furnace, the temperature and composition of the liquid product phases can be equated with those of the equilibrium conditions of the slagging zone, as discussed.

As the gases move upwards from the slagging zone, the Lumsden (1960) model first considers a hypothetical limiting case for a temperature interval, the furnace reaction zone, where the gas temperature falls from the slagging zone temperature of 1150°C to 1000°C, the temperature at which the rate of the rate-controlled carbon gasification reaction:

$$C + CO_2 \rightarrow 2CO \qquad \text{(6.5 repeated)}$$

falls to an insignificant level. For this particular case, all reduction reactions in the charge are considered to have previously taken place to completion higher in the furnace so that changes in the gas phase composition can be considered in isolation. In this temperature interval, reaction for Equation 6.5 is slow compared with rates of heat transfer so that the temperatures of the charge and gas are assumed to be the same at any particular location. As the gas temperature falls, reversion of the volatilisation reactions that have taken place in the slagging zone start to occur. The first effect is that lead sulfide is removed from the gas, being converted to lead metal and zinc sulfide:

$$ZnO\,(s) + PbS\,(g) + CO\,(g) \leftrightarrow ZnS\,(s) + Pb\,(l) + CO_2\,(g) \qquad (6.7)$$

This is the reverse of the reaction in Equation 5.2. A further fall in gas temperature then causes zinc vapour to react with carbon dioxide to form zinc oxide and carbon monoxide, reversing Equation 5.1:

$$Zn\,(g) + CO\,(g) \leftrightarrow ZnO\,(g) + CO\,(g) \qquad (6.8)$$

These processes continue until the temperature has fallen to 1000°C, by which time practically all the lead sulfide vapour has been removed from the gas, but most of the zinc vapour originally formed in the slagging zone still remains. Simple heat and mass balances can be derived, assuming that equilibrium still holds for the reversion reactions in this temperature range. The exothermic heat from reversion is balanced by the estimated heat required to increase the charge temperature and the endothermic heat required for the gasification reaction. The latter figure determines the amount of carbon consumed in reaction for Equation 6.5 additional to that contained in the gas generated in the underlying slagging zone. Figures 1 and 2 show the gas compositions as the temperature falls from 1150°C to 1000°C calculated by mass and heat balances per mole of carbon consumed in the slagging zone.

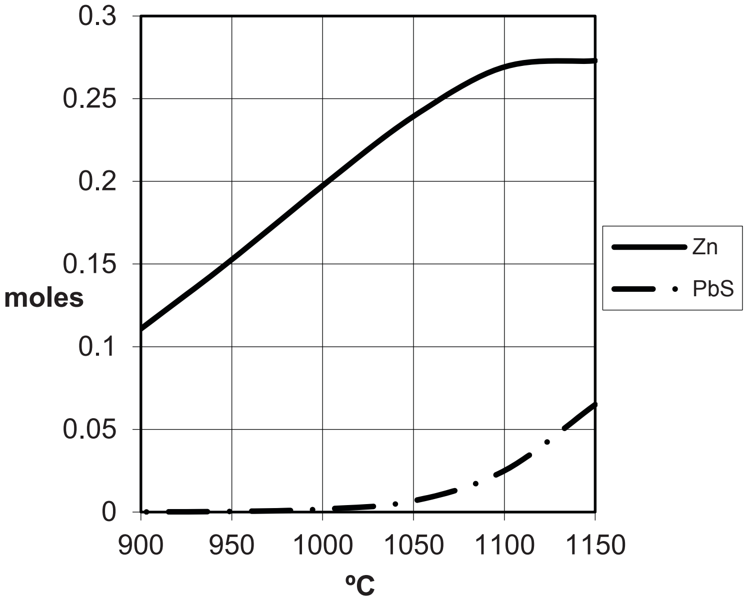


FIG 1 | Lead sulfide and zinc in the shaft gas, per mole of carbon burnt in the slagging zone (after Lumsden, 1960).

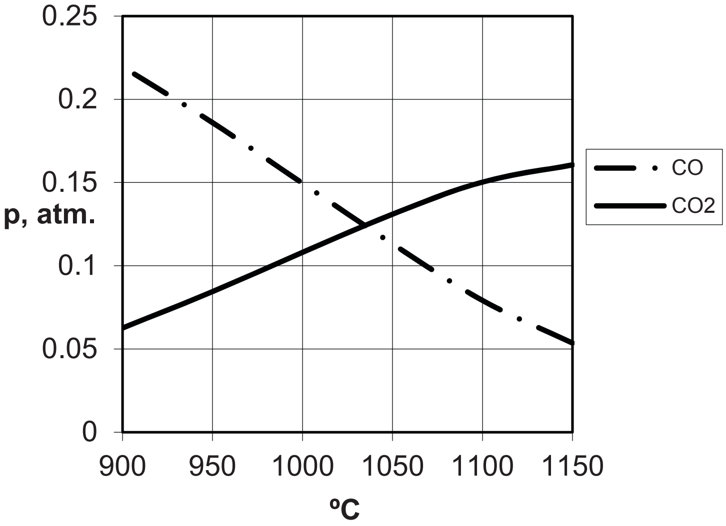


FIG 2 | Concentration of oxides of carbon in the furnace shaft when CO_2/CO in the slagging zone = 3.0 (after Lumsden, 1960).

By taking into account the kinetics of reaction in Equation 6.5 for the gasification of metallurgical coke, the residence time for the coke in the furnace reaction zone at the time of Lumsden's exercise is calculated to have been about 3.8 hours. Assuming that reactions in which carbon was consumed ceased at about 1000°C, the mass balance showed that the overall total carbon consumption per unit of slag produced was in accordance with production figures of the time. Lumsden considered that this was important evidence supporting the assumption of slagging zone equilibrium.

Figures 1 and 2 also demonstrate how the CO_2/CO ratio changes from the hearth equilibrium value of three to less than one as a result of both the temperature reversion of zinc vapour to ZnO and carbon gasification.

Although this case is hypothetical in that any rate-controlled reduction reactions are excluded from its thermochemistry, a similar calculation shows that an 'overcoked' situation in the hearth leads to lower CO_2 and higher CO and Zn vapour contents in the equilibrium gases entering this temperature zone. The resulting lower rates of the reversion reaction here push the inevitable exothermic reversion higher in the furnace, leading to the known hot-top operating condition – that is, high temperature and CO and Zn content in the exit gases, the only way the furnace can rid itself of the excess thermal energy. The argument holds even if reduction reactions are superimposed on the hypothetical base case.

Top reaction zone

Up to this point in his exposition, Lumsden assumed that all oxidised lead had been reduced higher in the furnace, thus disregarding any potential effects of its exothermic reduction in either the slagging zone or the furnace reaction zone. The context of the model description shows this was quite deliberate; Lumsden now wished to demonstrate the effects of different concentrations of oxidised lead in the sinter matrix on thermal distribution in the furnace shaft by determining the influence of a kinetic regime of oxidised lead reduction on the heat and mass balances from the exit of the reaction zone at 1000°C upwards. To do this, Lumsden proposed a model based on the relationship of heat and mass transfer between gas and charge phases. The sinter component was considered as a hypothetical mixture of PbO and slag to represent the real case where oxidised lead coexisted with slag components in several separately identifiable chemical phases (Manson, 1958). The thermochemical approach involved certain simplifying assumptions, some of which are considered in detail in the 1971 paper dealing with the chemistry of the zinc blast furnace (Lumsden, 1971). Others will be discussed later in this work in light of more recent experimental evidence.

Fundamental to both the 1960 and 1971 models was that the reversion reaction (Equation 6.8) only took place at a solid or liquid surface, for lack of a significant nucleation mechanism in the gas phase. Thus, heat was transferred from the gas to the solids, both by convection and by the mass transfer of reactants to the surface, such that the heat of reaction was transferred directly to the charge.

The Lumsden model related heat and mass transfer between gas and charge by calculating the vertical temperature and gas component concentration gradients in the following manner. If h is a coefficient with dimensions (distance^{-1}) applicable to both mass transfer and heat transfer, x represents distance upwards in the direction of gas flow, T represents temperature and g and s subscripts represent gas and charge:

$$\mathrm{d}T_g/\mathrm{d}x = -h(T_g - T_s) \tag{6.9}$$

and

$$\mathrm{d}p_g/\mathrm{d}x = -hD(p_g - p_s) \tag{6.10}$$

where:

p_g is the partial pressure of a molecular species in the gas

p_s is the partial pressure of that species at the surface of the charge

D is the ratio of the diffusivity of that species to the weighted mean diffusivity of all components of the gas

The main components of the gas are carbon monoxide and nitrogen, which have substantially the same physical properties so that for CO, D = 1.00; for the minor gases Zn and CO_2, it is estimated that D = 0.81 (Lumsden, 1960, 1971).

Two basic cases were then considered. When no oxidised lead was present at the surface of the charge (for example, when reduction was completed high in the furnace), the concentrations of CO, CO_2 and Zn vapour were those of the equilibrium of Equation 6.8 at the charge surface temperature T_s. When lead oxide was present, it was assumed that both Zn vapour and the CO were rapidly and completely consumed in reduction reactions so that their concentrations were zero at the charge surface. A further simplifying assumption used by Lumsden was that the charge consisted only of coke and sinter containing PbO (at unit activity) and slag components. By taking small increments in the solids temperature, the non-dimensional vertical distance *hx* could be calculated by heat and mass balance to produce profiles showing gas and charge temperatures, together with the concentrations of zinc vapour and PbO in the gas and charge respectively. An upper boundary limitation for the reduction of oxidised lead in sinter was that reaction ceases when the solid charge temperature reaches 600°C (as observed in practice).

The difference between cases where oxidised lead was absent from or present in the reaction system then allowed an assessment of the thermochemical behaviour of the hypothetical PbO/slag charge under different operating scenarios.

Figures 3 and 4 show profiles developed for gas compositions passing upwards from the furnace reaction zone at 1000°C; that is, at the point where the carbon gasification reaction was assumed to have ceased. The calculations are per mole of carbon consumed in the slagging zone equilibrium with a CO_2/CO ratio of 3 at a temperature of 1150°C.

Figure 3 represents an idealised case where PbO reduction took place only in the solid state. Given that the slag/carbon mass balance was for a sinter containing 0.5 moles PbO per mole carbon burnt at the tuyeres (that is, approximating operating conditions at Port Pirie in 1960), the curves show that even under the very favourable reaction kinetics imposed by Lumsden's assumptions, only about 70 per cent of the PbO could be reduced if reduction took place only in a charge solids temperature range from 600–800°C.

Figure 4 represents the case where reduction of PbO in the liquid state continued up to 1000°C. The break in the T_s temperature curve allows for the heat of fusion of PbO. This case shows that the reduction of PbO could be completed within the constraints of the assumptions.

An extension of this method of calculation suggests that if reduction of lead oxide continued until the charge temperature rose above 1000°C, the solid became hotter than

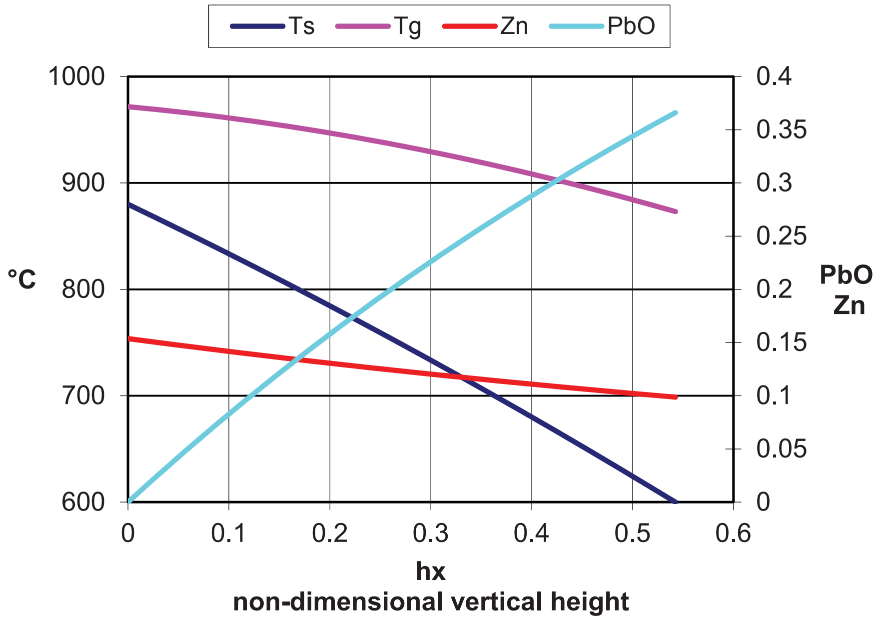


FIG 3 | Lead oxide reduction up to 880°C.
Tg = gas temperature, Ts = charge temperature, Zn = moles Zn in gas, PbO = moles PbO unreduced.

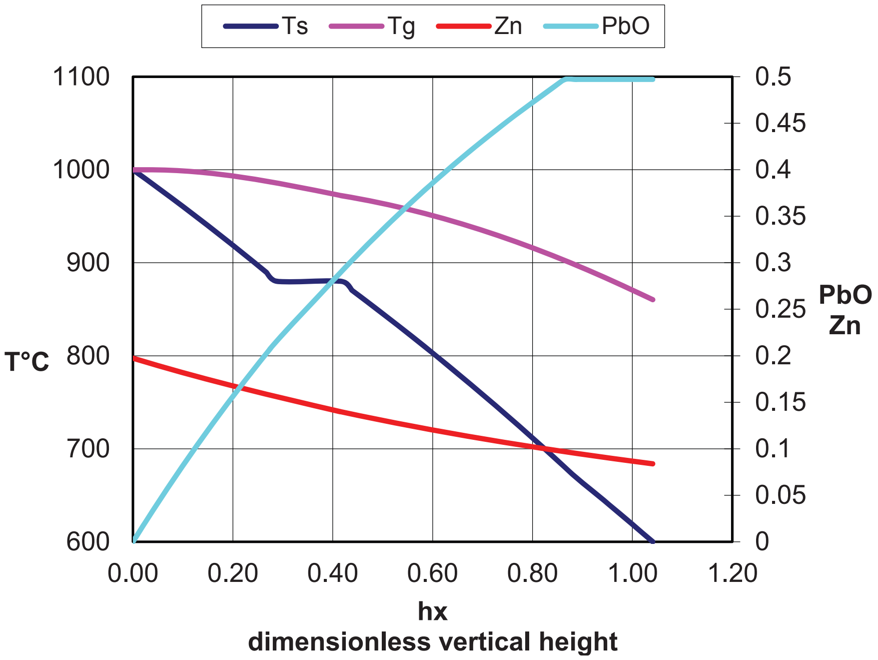


FIG 4 | Lead oxide reduction up to 1000°C.
Tg = gas temperature, Ts = charge temperature, Zn = moles Zn in gas, PbO = moles PbO unreduced.

the gas, as illustrated in Figure 5. Immediately below the level in the furnace where the reduction of lead oxide was completed, the solid was being cooled by the gas. Lumsden took this to mean that if there were any fusion of charge components at the highest temperature reached, the charge would freeze again as it descended in the furnace. This was proposed as the mechanism of bridging and hang-ups in the charge. By a further extension of this calculation, it was shown that the temperature reached during the reduction of the charge depended on the proportion of oxidised lead relative to slag and carbon in the input charge.

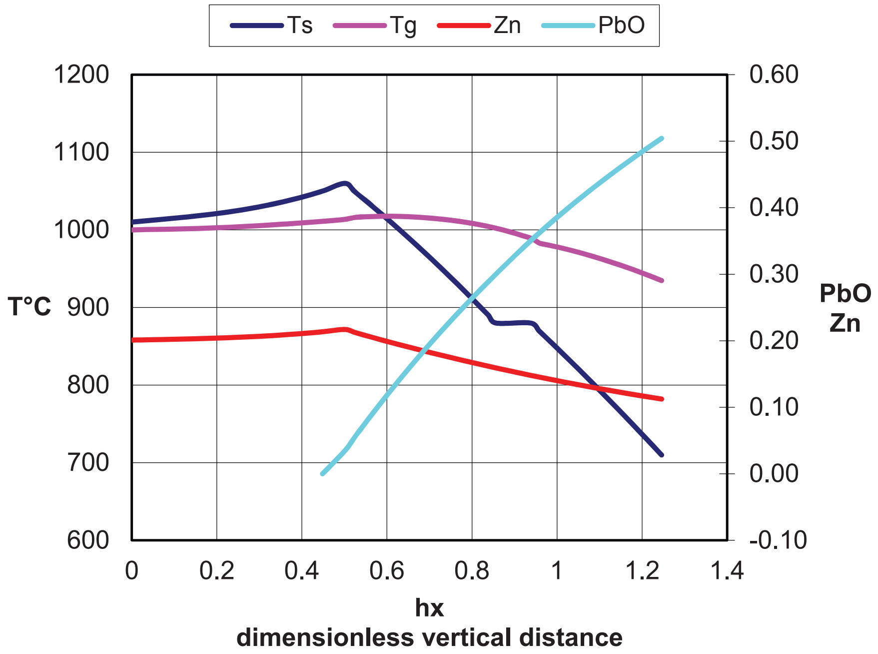


FIG 5 | Lead oxide reduction up to 1060°C.
Tg = gas temperature, Ts = charge temperature, Zn = moles Zn in gas, PbO = moles PbO unreduced.

Accordingly, this provided a theoretical explanation for the apparent limitation of the sinter PbO content that could be tolerated in practical lead blast furnace operation.

While this reasoning provided a conceivable explanation of phenomena occurring in the upper furnace reaction zone of the Port Pirie blast furnace, the context of Lumsden's paper reveals certain reservations relating to the actual mechanisms controlling the rates of chemical reaction there.

With the advantage of hindsight, the assumptions incorporated in the Lumsden model can now be examined:

- Very little of the oxidised lead component of the charge is in the form of free PbO available to react with reduction gases at the charge/gas interface. The majority is in a combined form, particularly in silicate glasses (Manson, 1958). It would be highly improbable that rate-limiting solid or liquid-phase diffusion of dissolved PbO to the reaction surface would not be a factor in the reaction kinetics. Furthermore, if it is necessary for the internal surface of a sinter lump to be readily accessible to the gas phase, a mechanism of pore diffusion would have probable kinetic implications if superimposed on that diffusion analogous to heat transfer to the outer surface.
- If diffusion of the reduction gas within the pores of the sinter is part of the overall reduction process, a reaction of PbO with Zn vapour such as in Equation 5.6 produces a solid ZnO product, which must inevitably occlude the internal reaction surface. It is quite possible, however, that reversion reaction according to Equation 6.8 occurs at the external surface, leaving ZnO at the surface and only its co-product CO diffusing into the porous inner surfaces. The thermal outcomes are numerically the same.
- While the analogy between heat and mass transfer can be expressed in terms such as those used in Equations 6.9 and 6.10, it is quite another matter to equate them through the use of a single constant coefficient 'h'. Heat transfer between a rising stream of hot gases and a descending packed bed of two solids (and possibly also liquid phases) with differing physical and thermal properties is a complex matter in itself, as demonstrated in the thesis by Zhao (1993). The resultant coefficient 'h' in this case is a temperature-dependent variable. Similar influences – gas phase fluid dynamics and temperature-dependent effects on component diffusivity in particular – may also be expected for diffusion of components from the bulk gas phase to the solid surface. The use of the single coefficient 'h' for both heat and mass transfer merely gives one solution for the relativity of physical heat transfer and the heat evolved by reduction reactions to the changes in temperature and composition of counter-current phases. Different values of 'h' for heat transfer and 'h' for mass transfer would result in different temperature and phase composition profiles. A resetting of 'h' values might be possible only if charge temperature profiles and gas analyses could be accurately established by experiment (an improbability to be discussed later); however, this would still require retention of the assumed diffusion rate limitation.

The model is therefore an over-simplified expedient to allow one mathematical solution to describe the reduction process. Overall, the reduction reactions, zinc reversion, carbon gasification and their associated thermal effects must all still occur within the residence time of the charge components and gas flows within the furnace. The problem is to establish where and how the relevant reactions take place and what the distribution of physical and chemical effects might be. Investigations carried out at Port Pirie and elsewhere are now discussed.

The Problem of Bridging in the Lead Blast Furnace

By the reasoning presented, the 1960 Lumsden model proposed an underlying and unavoidable thermochemical reason for the mechanism of bridging. This resulted essentially from the highly exothermic liquid-phase reduction of PbO at unit activity at the gas/charge interface by zinc vapour, together with the carbothermic reduction by CO at temperatures above 1000°C. These reactions were considered to cease as the PbO was depleted, allowing the charge temperature to fall to that of the gas phase with consequent refreezing of the partially liquefied charge, as seen in Figure 5.

Despite its plausibility, it is hard to argue a general case for the proposed Lumsden melting/refreezing mechanism. It can only be a selective theoretical consequence of the atypical Port Pirie practice that results in extensive exothermic reversion of metallic zinc vapour generated low in the furnace by reduction from slag of unusually high ZnO activity. Charge softening is a common characteristic of lead-zinc smelting furnaces using widely differing sinter/slag compositions. In the case of a quantitatively much smaller zinc recycle generated from lower zinc slags, the thermal outcome may well be insufficient to cause major fusion of the charge, although its softening temperature may be exceeded.

The paradigm at Port Pirie prior to Lumsden was that bridging was a purely physical process caused by softening and incipient fusion of the sinter at temperatures above the melting point of lead oxide as it passed downwards through the blast furnace thermal gradient. It was a factor of major commercial significance in that plasticity of the sinter, together with the relative sizing of sinter and coke, resulted in a restriction on charge permeability with consequent constraint on blast throughput. This in turn limited the coke combustion capacity and furnace productivity. Charge plasticity had been recognised in the investigation of North American lead blast furnace technology by Oldright and Miller (1936), but in that work and the subsequent evaluation by Ruddle (1957), wall accretion formation was considered as the major constraint on furnace throughput. Green (1977) makes no mention of charge fusion as a factor leading to charge bridging; he also clearly implied that accretion formation had been the major production constraint largely removed by the double tuyere configuration, which allowed a much greater operating width of the Port Pirie furnaces.

That sinter softening could be an important factor in furnace production efficiency was first articulated by Haney and Hopkins (1954) in discussing experiments at Port Pirie. Partial reduction of oxidised lead during the sintering process had been demonstrated in both laboratory tests and in operation to have raised the softening temperature. This had led to a view that if somehow the kinetics of the solid state reduction of sinter PbO could be enhanced within the blast furnace by increasing its available surface, the softening temperature of partially reduced sinter would be raised with beneficial effect on furnace performance. Laboratory-scale sinter reduction tests with CO and hydrogen reductants had suggested that with granular samples, reduction commenced at about 450°C and at higher temperatures took place rapidly and uniformly throughout the sinter matrix, leading to conjecture that sinter had a microstructure readily accessible by reducing gases. A subsequent project was sponsored at the University of Adelaide to examine whether the 'reducibility' of lump sinter produced on the sintering machine could be enhanced by increasing its accessible reaction surface to maximise the solid-state reduction of its oxidised lead content (Ward, 1959). The project failed in that strong, well-fused sinter giving good furnace performance proved not to have a highly available internal surface area. Conversely, sinters with high surface areas and reducibility were poorly fused, friable and liable to unacceptable breakage in the multiple mechanical transfers involved in moving sinter from the sintering machine to the blast furnace in the plant layout at Port Pirie.

The importance of sinter strength was demonstrated at Port Pirie by ongoing developments in updraught sintering operating practice described by Grant and Cunningham (1971). Following trends in blast furnace practice in the iron and steel industry during the 1960s, where productivity had been improved by using smaller and more uniformly sized feed, significant furnace productivity gains were made at Port Pirie by interrupting the updraught on one or more of the sintering machine wind boxes soon after the point of flame breakthrough. This caused the structure of the hot sinter to collapse to some extent, becoming more dense without losing its cellular structure. This stronger sinter could be broken to a smaller size without producing excessive fines (necessarily returned to the sintering operation), as well as allowing a closer sizing of the furnace feed. The production of large-sized brittle sinter whose attrition during handling produced unwanted fines in the furnace feed was significantly reduced. Effectively, this development was quite contrary to the postulates of Haney and Hopkins and the University of Adelaide project.

Rather than trying to enhance the kinetics of the solid state reduction of the sinter within the blast furnace, the beneficial effect of partially reducing the oxidised lead content of the blast furnace feed sinter by adding coke breeze to the sinter machine feed was confirmed by statistical examination of sintering/blast furnace performance by Grant and Cunningham (1971). The optimum oxidised lead content of sinter feed to the blast furnace was consistent with the Lumsden model calculations, although practice at Port Pirie was influenced by other commercial and environmental considerations.[3]

The Grant and Cunningham paper confirmed that furnace throughput was strongly correlated with the blast air and coking rates, consistent with the known production-limiting effect of coke combustion capacity. After excluding the overwhelming masking effects of coke and air rates as not independent of sinter properties, the chemical and physical properties of input sinter were found to be significant determinants of the production rate, resulting in operational changes to achieve an optimum throughput outcome. The statistical regression equations, however, only explained 22–25 per cent of the total variance in the production rate. What could not be accounted for in investigating the effects of input sinter properties on furnace production rate were the internal physical constraints on gas flow within the furnace due to (historical) accretions and partial or localised charge fusion. Although charge fusion is partly dependent on the combined lead

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[3] In the late 1950s, coke breeze was a cheap commodity stockpiled at Port Pirie from the screening of coke shipments to provide an appropriately sized blast furnace feed; however, this internally generated material was insufficient to provide ongoing requirements for the preferred sinter plant operation so that other sources involving external purchasing cost and long-distance transport became a factor. Furthermore, the practice was shown to affect the operation of the contact acid plant associated with the sinter plant by reducing the O_2/SO_2 ratio of the acid plant feed gas to the detriment of conversion efficiency.

content and sizing variables found to be significant in the statistical investigation of sinter properties, it is also dependent on thermal inputs relating to zinc reversion and exothermic reduction reactions derived from hearth conditions associated with the excluded blast air and coke rates. Grant and Cunningham (1971) also acknowledged that intervention by operators in order to moderate adverse furnace conditions was a confounding factor affecting the statistical investigation. Given these unknowns and the experimental difficulties in quantifying many of the variables under examination, the limited variation explained by the investigation was considered satisfactory.

After Lumsden (1960), the underlying thermal effects associated with zinc recycling resulting inevitably in charge softening were generally accepted at Port Pirie. An even distribution of coke throughout a charge column, by volume largely composed of sinter, was considered an important factor in bridging control (though difficult to achieve in practice) – a view repeatedly expressed in lead smelting literature since the days of the earliest authors (1890 onwards). Experimental investigations to determine the reasons for charge softening as the underlying cause of furnace bridging were never seriously revisited at Port Pirie during the 1960s and 1970s, although this had been the ostensible reason for the work originally undertaken in the 1950s described by Haney and Hopkins (1954). It is therefore of interest to consider evidence from investigations at other operations.

Sinter softening studies together with optical microscopy were carried out at Sulphide Corporation (Holliday, Shoebridge and Firkin, 1980) on ISF sinters and at Mt Isa Mines (McLoughlin, Riley and McKean, 1980) with lead blast furnace sinters. Both show the importance for blast furnace performance of containing potentially low-melting point lead silicate glasses within an interlocking matrix of high-melting crystal phases such that the softening point of the sinter mass is maintained at temperatures above the melting point of the glasses. The compositional differences between sinters for the ISF zinc blast furnace and the lead blast furnace were such that the supporting crystal structures had different mineralogy. In the case of the Mt Isa lead blast furnace, the important solid-phase minerals were zinc spinels (franklinite) and melilites (hardystonite). In the ISF sinters the high zinc content also resulted in the precipitation of acicular crystals of zincite, the shape of which was an important factor in maintaining a high softening temperature. In each case, however, if the sinter composition and sintering conditions were such that the glass phase became continuous within modified and rounded crystal structures, the softening temperature was drastically lowered with consequent effect on furnace performance.

Hollitt (1992) considered the differences between the Mt Isa and Port Pirie sinter/blast furnace practices in light of the higher slag zinc content to facilitate the slag fuming operation at Port Pirie. It was contended that suitable solid zinc-bearing phases (for example, the spinel franklinite and the melilite hardystonite) were formed in the Port Pirie sinter to give good blast furnace performance. Manson (1958) had earlier identified such melilite and spinel structures in Port Pirie sinters by microscope examination.

All these studies point to low-melting calcium-lead-silicate glasses as the important contributor to low-temperature sinter softening, with calcium (or in the Port Pirie case, zinc oxide as well) as an important agent in raising the glass fusion temperature.

More recently, Zhao *et al* (2008) carried out phase equilibrium studies using the FactSage® program on melts with compositions corresponding to production sinters from three sites, as well as two slags synthesised to replicate the first stage product from the two-stage lead smelting ISASMELT™ process. These showed that the observed formation of spinel and/or melilite on cooling is thermodynamically predictable. Observed phase assemblages were explained by using a pseudo ternary $ZnO–Fe_2O_3–(PbO+CaO+SiO_2)$ sectional phase diagram on which all the experimental materials could be located and compared.

This paper also presents the results of the comparative softening behaviour of two of the materials, a Mt Isa sinter and a synthetic ISASMELT™ slag. The slag softened at 980–1020°C, the sinter at 1120–1130°C. Micrographs of the two materials show the sinter with an interlocking crystal structure and no continuous glassy phase. In the case of the slag, the glassy phase was continuous, both in slow and rapidly cooled regions. The relative softening behaviours were therefore consistent with the earlier structural observations of McLoughlin, Riley and McKean (1980), who had also noted that low softening-point sinters related to poor blast furnace performance. No discussion of softening behaviour was made in relation to the main thrust of the paper, which was to consider the reduction behaviour of all five materials under laboratory conditions as a means of assessing their potential industrial performance.

The possibility that the physical softening leading to potential fusion of the major charge component could in itself form a major constraint on furnace productivity did not seem to be appreciated by Zhao *et al* (2008). The conclusion reached in this paper, as well as subsequent identical conclusions by the same authors (Zhao *et al*, 2010), was that slags of chemically similar constitution to those used in their experiments would be suitable as a lead blast furnace feed material. This ignores the potential constraints presented by their physical constitution. It is to be noted, however, that these experimental slag samples were synthetic, so it is entirely possible that their physical structure could differ significantly from that of slags formed under industrial conditions. The rate of cooling from the molten state is likely to be a significant factor in developing a critical interlocking structure. As always, the suitability of a given feed can be justified only by appropriate field experimentation.

Direct evidence in favour of a general softening mechanism comes from the experiments at Chimkent in which the shaft contents of an operating pilot-scale blast furnace were frozen by replacing the blast air with nitrogen (Polyvyannyi *et al*, 1971). The furnace contents were sectioned, examined and analysed to establish a vertical charge composition profile. During operation, the furnace used high coke and blast rates, such that there was no centre-line accretion. From an experimental point of view, this allowed consistent gas temperature and vertical centre-line CO_2/CO profiles measured during the operating period to be matched with later examination of the solidified charge. The input sinter contained 42 per cent total lead and nine per cent total zinc – a ratio perhaps not greatly different from that at Port Pirie. The CaO/SiO_2 ratio in the sinter was 0.55. The course of reduction of individual lead species in the sinter together with measured gas temperatures is shown in Figure 6.

Contrasting with the findings of Madelin, Sanchez and Rist (1990) – who discovered no suggestion of a constant-temperature 'thermal reserve' region during their lead blast furnace investigations at Noyelles Godault – the Chimkent experiments found that over a vertical height interval of 2 m commencing at 1.15 m upwards from the tuyere axis, the gas temperatures remained fairly steady at 1020 ± 20°C. The frozen charge from within this gas temperature range was described as follows:

> *At a height of 2.5–2.8 m above the tuyere centre-line the sinter was somewhat compacted, although it all still remained porous (the gas temperature in this zone was 800–900°). Lumps of coke in these horizons were rounded to a significant extent. At the 2.5 m level droplets of lead (0.5–2 mm diameter) were apparent on the lumps of sinter. At a height of 2 m in the centre of the furnace the sinter became dense and of low porosity; the distribution of coke was more uniform than in the upper horizons.* (Polyvyannyi *et al,* 1971).

Thus, compaction became more noticeable as the sinter travelled down the furnace, presumably under the influence of rising solids temperatures (although no determination of a solids temperature gradient was experimentally possible). There was no evidence of complete fusion of lead silicate phases into a separate homogeneous molten phase and the charge material was still described as sinter. The lead tenor of the sinter was still high, falling only from 34 per cent (eight per cent in metallic form) to 28 per cent (13 per cent metallic). At 1100°C, Polyvyannyi *et al* (1971) stated that at this level the slag content of the unreduced sinter had not fused and separated, and 20–30 per cent of the lead remained unreduced. In a later, more detailed microscopic examination of these charge sinter structures, Polyvyannyi (1976) identified localised formation of the first slag-containing systems in the solids from a zone corresponding to a gas temperature of 840°C. As the sinter moved downwards, the appearance of liquid phases, the rate of slag formation and final slag production increased to completion in the tuyere zone. The majority of the remaining oxide lead was considered to be reduced from the liquid state in the tuyere zone at 1180–1270°C, with some phase separation of slag and bullion taking place there and below the tuyeres. Softening experiments reported in the 1976 monograph again showed that the initial softening temperature of residual charge materials increased from about 800°C for unreduced sinter to about 950°C for reduced materials from the tuyere zone.

While the Lumsden model calculations suggest a similar hiatus in the gas temperature gradient to that actually observed at Chimkent (Table 1 and Figure 6), the results of Polyvyannyi *et al* (1971) indicate that reduction of oxidised lead species under the Chimkent pilot plant conditions was relatively slower than that predicted by the mechanism assumed by Lumsden. The significantly higher specific smelting rate (measured in t/m^2.day) in the Chimkent pilot tests, with the correspondingly lower residence time of sinter in the furnace (by a multiple estimated from data in the Polyvyannyi *et al* (1971) paper of about 2.5 times less than that in the Port Pirie regime) is a confounding factor, as is the lack of any evidence as to the temperature profile of the sinter as distinct from that of the gases.

The Chimkent results do show, however, that different chemical species in the sinter are reduced at different rates in the lead blast furnace shaft, indicating that the Lumsden model assumption that all oxidised lead species in the sinter can be considered as PbO is an oversimplification. Furthermore, the rate of lead reduction was overestimated in

TABLE 1

Change in phase composition of lead sinter by horizontal level in the Chimkent Pilot Furnace (Polyvyannyi *et al*, 1971).

Horizon	Concentration of form of lead (%)							Concentration of form of zinc (%)						Temp (°C)
	Sulfate	Silicate	Ferrite	Metallic	Sulfide	Oxide	Total	Sulfate	Silicate	Ferrite	Sulfide	Oxide	Total	
I	0.10	27.00	3.34	2.38	2.35	5.33	40.45	0.015	2.00	3.77	1.71	1.37	9.00	396
II	0.09	27.12	3.27	2.34	2.38	5.41	40.61	0.18	2.02	4.24	1.78	1.39	9.61	518
III	0.10	26.95	2.61	3.36	2.41	4.55	39.98	0.02	2.16	4.66	1.61	1.27	9.20	647
IV	0.08	25.82	1.63	5.09	2.08	3.47	38.17	0.016	1.80	5.05	1.77	1.43	10.21	728
V	0.06	23.89	1.06	5.70	1.82	1.97	35.50	0.014	2.17	4.96	1.90	1.61	10.77	887
VI	0.05	20.64	0.57	8.22	1.57	1.05	32.30	0.012	2.38	5.50	2.13	1.77	11.80	1008
VII	0.04	16.92	0.34	10.98	1.40	0.79	30.13	0.011	2.57	4.68	2.01	2.73	11.10	1022
VIII	0.03	14.35	–	12.70	1.34	–	28.42	0.01	2.93	3.92	1.87	1.67	10.49	1040
IX	0.02	11.54	–	13.99	1.14	–	26.69	0.007	2.96	3.78	2.06	1.46	10.33	1186
X	–	8.00	–	15.09	1.48	0.53	25.10	0.004	2.97	3.62	1.94	1.13	9.70	1270
XI	0.10	4.04	–	15.34	1.68	0.27	21.88	–	3.24	3.34	1.65	0.81	9.04	
XII	0.07	1.61	–	13.28	2.44	–	17.40	–	3.29	2.82	1.50	0.41	8.12	

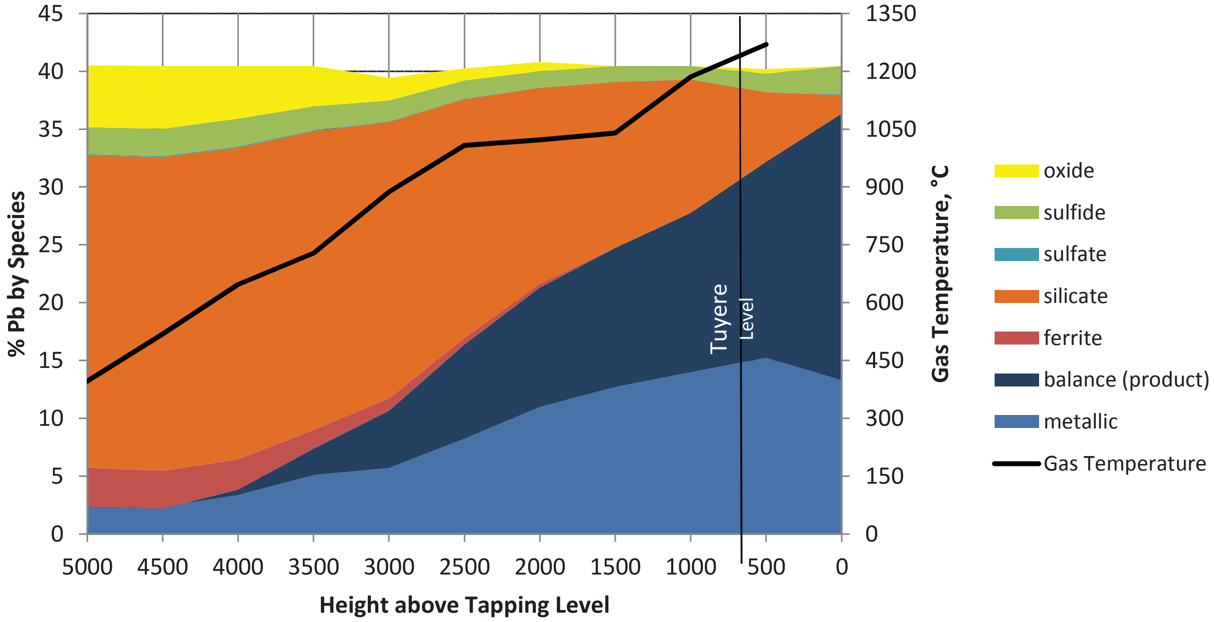

FIG 6 | Change in lead species within charge burden. Chimkent pilot-scale lead blast furnace trial (after Polyvyannyi *et al*, 1971).

the Lumsden model, as will be shown in considering experiments relating to the kinetics of sinter reduction subsequent to 1958. Nevertheless, because there is a temperature gradient, the thermochemistry of reversion of zinc vapour must still hold, explaining the hiatus in the slope of the gas temperature gradient in Figure 6, during which interval there would be little or no direct heat transfer from gas to solids. Lumsden's model suggests that heating of the charge in this zone of almost constant gas temperature would be due to both zinc reversion and exothermic oxide lead reduction as shown in Figures 4 and 5. Reversion of zinc was confirmed in the Chimkent trials by an increase in the zinc oxide and zinc ferrite content of the sinter charge materials at mid-furnace levels (Table 1). That the Chimkent results show that lead silicates can persist right up to an equilibrium temperature of 1150°C demonstrates that a reworking of the equilibrium model is required, taking into account the kinetics of reduction of lead compounds as well as carbon gasification. The Polyvyannyi papers yield no evidence to support or deny Lumsden's postulate that the solids temperature may exceed the gas temperature because of exothermic zinc reduction of oxidised lead.

Evidence will be presented later that low-melting and easily reduced lead ferrite and free PbO in a sinter represent the excess of lead present above that which can be accommodated in compounds formed with slag-forming flux constituents under the oxidising conditions of the sintering operation. Lead silicates of highly variable composition and fusion temperatures are the major lead phase present. It is logical that the explanation of bridging in the lead blast furnace shaft should be the gradual softening and compaction of the furnace burden as its temperature rises through the melting point of glassy lead phases held within a lattice of high-melting crystal phases. The actual softening temperature will depend on the degree of reduction of lead compounds that can occur at low temperatures, both in solid and in liquid states.

Nevertheless, the thermochemical arguments of Lumsden must still hold.

Successful blast furnace operation therefore requires an appropriate balance between reduction kinetics and thermodynamics such that temperature effects on the bridging tendencies of the charge (that is, the physical factor governing lead blast furnace performance) are held to acceptable levels. From a theoretical viewpoint, the question is whether the kinetics of carbothermic reduction of lead sinters can be sufficiently defined over a range of temperatures and degree of reduction to allow the determination of the associated thermal effects. Solid, liquid and gas phase dynamics are also involved. Modelling studies to date have tended to concentrate on one aspect or another, but not all. Thus, Lumsden's model considered the thermochemistry with only rudimentary assumptions as to kinetics. Several studies – some quite recent – have attempted to define the reduction kinetics without fully considering the thermochemistry of molten oxide phases and slags, as well as the implications of the zinc volatilisation accepted as essential to the Imperial Smelting and slag fuming processes.

These studies will now be considered in rough chronological order, taking into account investigations at other sites and by other organisations, as well as those by BHAS at Port Pirie.

The Kinetics of Reduction of Lead Sinters

8

Port Pirie laboratory experiments reported by Haney and Hopkins (1954) did not lead to any specific evaluation of kinetic parameters for the heterogeneous reactions of solid and incipiently molten sinter with a reducing gas. Nevertheless, certain observations were made that have some bearing as to the mechanism of reduction, influencing Port Pirie thinking for some years to come. In summary:

- Reduction experiments were carried out at temperatures of up to 850°C on sinter samples crushed and screened to 3–5 mm using a gas mixture of 17 per cent CO and 83 per cent N_2.
- Reduction commenced at a temperature of about 450°C as indicated by globules of lead on the surface of the sinter granules.
- Reduction was more vigorous at 650°C. When activity had apparently ceased, examination revealed globules of lead within the inner structure of the granules, indicating deep penetration by the gas.
- When reduced granules were broken and resubmitted to further reduction, activity was renewed, suggesting exposure of fresh surfaces.
- By comparison, sinter ground to <0.15 mm, briquetted, then broken to granules 3–5 mm showed increased rates of reaction as well as increasing the overall extent of reduction compared with the 'solid' sinter.
- Reaction rates decreased at temperatures of about 750°C; that is, near the fusion temperature of lead silicates, increasing again in tests at 850°C and above.
- Some of the differences in the reduction rate appeared, statistically, to relate to changes in sinter charge preparation.

It was postulated from these observations that developments leading to an increase in available surface area would bring about significant improvement in furnace capacity and thermal efficiency. With the advent of updraught sintering at Port Pirie in 1956, the consequent marked reduction in blast furnace productivity and efficiency led to a renewed interest in the manner in which sinter plant operating practice might affect sinter surface area and hence its low temperature reactivity.

The project sponsored by BHAS in 1956 at the University of Adelaide employed facilities for measuring the specific surface area of solids by the Brunauer–Emmett–Teller (BET) method. Used before the advent of commercially available instruments, the apparatus was based on that pioneered by the innovators of the BET surface adsorption technique. Both conventional nitrogen and krypton adsorption could be used, the latter offering certain advantages in precise measurement on solids with relatively low surface areas. Experimental sinters prepared in the BHAS laboratory under various possible operating conditions were evaluated by reactivity and surface area measurements (Ward, 1959).

The project was a follow-up of the reactivity/softening temperature ideas of Haney and Hopkins aimed at the empirical enhancement of blast furnace performance. The roles of heat and mass transfer as well as reduction chemistry were known to be involved, but with only rudimentary understanding at that time. The measurements of chemical 'reducibility' were therefore not intended to produce rigorous chemical kinetic parameters, but merely indicate whether the low-temperature reduction behaviour of sinter could be favourably influenced by sinter plant operating practice. As with the earlier work, however, some further suggestions as to the mechanism of low-temperature reduction of sinter can be gleaned from the results.

Considering, firstly, the variation of the specific surface area (SSA, m^2/g) of two separate, crushed sinter samples with a screen fraction size as shown in Figure 7, it can be calculated that the measured SSA is about four orders of magnitude greater than solid spheres of equivalent particle diameter. Secondly, extrapolation to a smaller particle size indicates that size comminution exposes an increased internal surface area in agreement with the findings of Haney and Hopkins. Thirdly, the shape of the curves suggests an asymptotic approach to a limiting surface area at some undefined large particle size, possibly that of lump sinter charged to the blast furnace, but this cannot be estimated from the limited sample and particle sizing that could be assessed within the equipment used in these experiments.

Figure 8 shows that the specific surface area of a given sized sample increases as reduction proceeds. Since the rate of reduction decreases at the same time, it is concluded that while the increase in surface area may partly be due to the exposure of a new reducible surface (for example, as in a shrinking core model of a gas-solid reaction), it is more likely a result of removing oxidised lead from initially exposed sinter components within the lattice structure. This is consistent with the findings of Haney and Hopkins, who found that reduced samples could be further reduced after crushing.

It was proposed in this project to devise a single, consistent measure of 'reducibility' that could relate to both the specific surface area on one hand and, on the other, the operating parameters employed in producing on a small laboratory pilot-scale sinters of differing physical and chemical properties, as described by Manson (1958). Tests were carried out

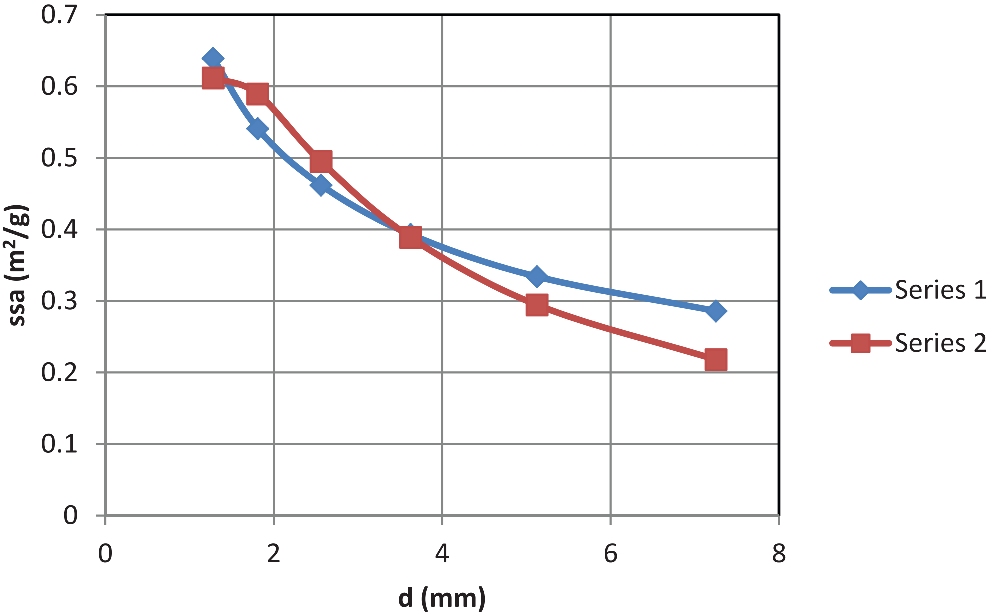

FIG 7 | Typical Broken Hill Associated Smelters (BHAS) sinters 1958 – specific surface area versus nominal particle diameter.

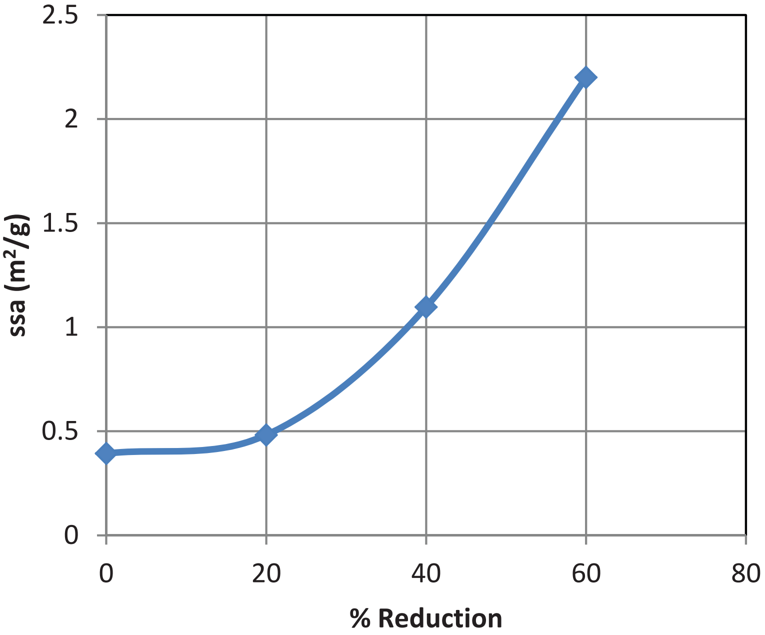

FIG 8 | Typical Broken Hill Associated Smelters (BHAS) sinter 1958 – change in surface area with reduction.

with both hydrogen and carbon monoxide reductants over a temperature range of 500–800°C with a range of particle sizes. Following similar developments in the iron industry, a reproducible, standardised experimental procedure was developed using pure hydrogen as the reductant at 600°C with a sample sized to the British Standard specification screen -72# + 100# screen fraction. The percentage reduction could be plotted as a function of time using the weight of product water formed, the weight of metallic lead formed or the decrease in the weight of reducible oxidised lead (considered as acetate-soluble oxide, silicate and sulfate) as criteria by which the percentage reduction could be calculated. Following the literature, calculated reducibility indices were the time taken to reach 80 per cent reduction or the area under the per cent reduction/time curve to 60 minutes. These indices correlated well with each other and with measured values of the specific surface areas – surprisingly so, since the amount of water formed during hydrogen reduction certainly included that produced under the conditions of the tests from other species such as iron and zinc compounds. This would suggest either the unlikely possibility that all reducible compounds were reduced at the same rate, or else the rate-limiting factor was not related to the chemical kinetics of reduction of the individual species so much as a purely physical factor, such as the rate of diffusion of the reductant gas through the porous solid to the reacting surface. Such a mechanism would be consistent with observed differences in the reduction rate between hydrogen and carbon monoxide reductants, and with different rates for reductant mixtures of reductant and nitrogen. This work may also have justified the assumption of diffusion rate control for low-temperature solid-state reduction in the subsequent Lumsden (1960) blast furnace model.

The two recent papers by Zhao *et al* (2008, 2010) comparing the reduction behaviours of three industrial sinters and two slags simulating those produced in the first stage of the ISASMELT™ process are identical, with the exception that the section on comparative softening behaviour in the 2008 paper (discussed earlier) was omitted from the 2010 paper. Specific references as to the sources of the materials were omitted from the later paper. Laboratory experiments were carried out on all five materials to compare their behaviour during reduction by CO gas at 100°C temperature intervals between 800°C and 1200°C. A common reaction time of 30 minutes was chosen and the course of reaction followed as the percentage change in weight of the samples. The reaction sequence at higher temperatures was interpreted in terms of equilibrium outcomes predicted by FactSage®. While some differences between the various materials were noted as to the degree of reduction achieved at the different temperatures – suggested by the authors as due to variations in porosity – all materials were completely reduced at the highest temperatures, leading to a conclusion that ISASMELT™ slags could be advantageously treated in a lead blast furnace. The extrapolation from laboratory results produced under artificially controlled conditions bearing no resemblance to those encountered in an industrial furnace is perhaps hard to justify. In particular, the laboratory use of pure CO as the reductant led to the *reduction* of zinc from the sample under the experimental conditions (that is, a weight loss), whereas the Lumsden approach postulates *re-oxidation* of zinc from gas at a CO_2/CO ratio of 3 with a CO partial pressure of about 0.05 generated by an equilibrium between slag and hearth gases low in the blast furnace, resulting in a potential weight gain. It must be concluded that these tests are not necessarily relevant as a predictor of the blast furnace behaviour of potential charge materials.

Laboratory investigations into the reduction of individual oxidised lead components of sinter were undertaken in conjunction with the pilot smelting trials at the Chimkent lead plant, whose changes in charge composition with depth and gas temperature are presented in Figure 6. Subsequent to the trials, further laboratory investigations were carried out into the kinetics of reduction of input sinter and samples taken from various levels of the furnace after the trials. All work was collated in Polyvyannyi (1976).

The overall aim of the Chimkent trials was to try to evaluate the use of oxygen enrichment and natural gas together with preheated blast in the lead blast furnace. Here, the laboratory investigations were aimed at determining the kinetic parameters of reduction of pure lead compounds by hydrogen, carbon monoxide, solid carbon and natural gas at temperatures up to 1000°C. The pure compounds chosen for investigation were those identified in production sinter by infrared spectroscopy – specifically lead oxide, lead ferrite $PbO.2FeO$, and the lead silicates $PbO.SiO_2$, $2PbO.SiO_2$ and $4PbO.SiO_2$ in glassy form. In order to reduce potential diffusion effects within the solid state, all compounds were in powdered form at less than 0.075 mm in diameter. The results showed that reduction in the solid state of lead oxide followed first-order kinetics. For the lead silicates, first-order kinetics were followed up to approximately 20–30 per cent reduction. Beyond that, deviation suggested increasing occlusion of the surface by siliceous reaction products. In all cases, the variation in reaction rate with the increasing degree of reduction took the form:

$$M = \frac{1}{t}\ln\frac{1}{1-x} - \beta^{x/t} \tag{8.1}$$

where:

M is the effective rate constant depending on the degree of transformation

$\frac{1}{t}\ln\frac{1}{1-x}$ is the rate constant for a first-order reaction

x is the degree of transformation at time t

β is the coefficient of retardation

Using this equation still allowed an evaluation of energies of activation for the reductions. In the case of the silicates, a significant retardation in reaction rates in the liquid state (above 800°C) was considered to be due to liquid-phase diffusion effects rather than any change in energy of activation.

The so-called ‘direct reduction’ of lead silicate glasses by solid carbon is discussed both by Polyvyannyi, Vasilieva and Ivakina (1971) and in Polyvyannyi’s subsequent 1976 monograph. Solid phase reduction of the glasses by carbon was negligible. The liquid-phase reduction of the silicates by powdered carbon was, initially, considerably faster than by the gaseous reductants, as reflected by lower activation energy (34–38 kJ/mol compared with 100–130 kJ/mol at up to 20 per cent reduction in the range 800–1000°C). The difference was ascribed to diffusion influences, which were explored more fully in the 1976 monograph. The participation of CO regenerated via the reaction of product CO_2 with the carbon surface was acknowledged, but the overall process was still referred to as 'direct reduction'. As reduction progressed, the deviation from first-order kinetics in accordance with Equation 8.1 was ascribed to the build-up of product silica in the melt, changes in viscosity and reduction of the carbon contact area. In later experiments, the addition of calcium oxide to the lead silicate melt was shown to enhance the initial rate of reduction by carbon. Comparison of the results of the pilot trial shown in Figure 6 with the laboratory data showed qualitative agreement with respect to the sequence of reduction (ferrite, oxide, silicate and lead silicate glasses).

Polyvyannyi (1976) describes further laboratory investigations into the kinetics of the molten-state reduction of lead silicate glasses up to 1200°C. The reduction of sinter samples, both input sinter and reduced sinter from different levels in the frozen pilot-scale burden, is also described, in particular those from which the easily reduced components – free PbO and $PbO.Fe_2O_3$ – had disappeared. From this work, it was concluded that a correlation – existing between the composition of the sinters, the content of lead glasses, the rate constant for reduction and the magnitude of the energy of activation – demonstrated chemical control of the kinetics of reduction by carbon monoxide.

The kinetics of reduction of sinter by carbon powder in this later, higher-temperature work were shown to be not significantly different from those by carbon monoxide. The 1971 paper claimed that the apparent increase in the rate of reduction of molten silicates towards and within the tuyere zone of the Chimkent pilot-scale furnace was due to direct reduction by the carbon. The 1976 monograph suggests that the acceleration was purely a temperature effect and there could be no distinction between interfacial reduction by gaseous carbon monoxide and direct reduction on carbon surfaces. Laboratory studies of silicate reduction within powdered sinter samples by carbon deriving only from graphite crucibles at temperatures of 1000°C and above revealed penetration and reduction by CO, as well as reduction at the carbon interface. On the much larger scale of the pilot furnace, descriptions of the charge after freezing showed that the residual sinter retained a coherent structure down to within 0.5–0.7 m of the tuyere axis level (gas temperature 1050–1100°C). The coke was only slightly enriched and uniformly distributed within the charge. This suggests that molten silicates were not released to pass over a majority carbon phase in such a way as to allow direct reduction by the carbon surface as a major reduction mechanism.

In comparing the results of pilot-scale experiments with laboratory results, Polyvyannyi (1976) further claimed that given the change in gas compositions and temperatures from the 1000°C zone down to tuyere level, there was qualitative agreement of the data with respect to the sequence of reduction of the lead oxides (ferrite, oxide, silicate and lead silicate glasses) and to the degree of transformation. It is hardly to be expected, however, that data from the very small-scale laboratory experiments could be extrapolated to industrial-scale practice. Powdered samples deliberately used for solid-state reduction experiments were chosen to eliminate any influence of solid-state diffusion to the reaction surface that might be expected in operational sinters. For reduction experiments above the melting point of the lead silicate glasses, fine grinding of the input samples might have been expected to destroy the solid-state crystal structures supporting the liquid-phase reducible lead compounds, thus facilitating contact with the solid carbon reductant. Yet the porosity of the quenched product indicated that reduction gases were able to penetrate the presumed semi-molten mass of sinter, and product gases were able to escape.

In investigations into the kinetics of reduction of lead-bearing melts in the Kivcet process, the carbon surface was considered not to be 'wetted' by the melt; instead, reduction proceeded via a cyclic process in the gas film between melt and carbon in which the active reductant, CO, was regenerated by the reaction of product CO_2 at the carbon surface (Lyamina and Shumskii, 2003). As shown by Kinaev, Jak and Hayes (2005), the reaction rate was clearly defined not only by the PbO activity of the melt and the CO partial pressure (that is, chemical rate control), but also the interfacial area between melt and carbon. Migration rates of PbO to the reaction surface were not significant, nor was the type of carbon. A comparison of these findings with those of Polvyannyi's laboratory reduction experiments under fixed conditions suggests that the effect of the interfacial area was not taken into account in his kinetic data. His laboratory kinetic data cannot be used predictively to determine absolute rates of reduction that can be extrapolated to the widely differing conditions of pilot- and industrial-scale experimentation.

A further question arises as to whether the results of the Chimkent laboratory and pilot blast furnace experiments can be generalised to allow the development of a mathematical model of the Port Pirie furnace chemistry, as has been attempted by Zhao (1993). The Chimkent pilot furnace used a coke/product lead ratio 50 per cent higher than at Port Pirie. The mass balance dictates that the gases generated in the tuyere zone would have been very high in CO content, much higher than suggested by cited oxygen partial pressures in typical industrial lead blast furnace practice. Burden samples showed evidence of zinc recirculation without allowing quantification of its magnitude or effect on heat and mass transfer. Residence time of sinter in the Chimkent pilot furnace was less than half that at Port Pirie. Potential segregation of sinter charge and coke seems to have been avoided in the pilot experiments, allowing centre-line gas temperature and composition measurements to be taken as a reasonable representation of average conditions in cross-sectional profiles under stable smelting conditions. The typical variability of the top conditions in the Port Pirie furnace has been commented on elsewhere. The Port Pirie use of partial sinter reduction on the sinter machine results in a somewhat lower oxidised lead content in the charge and hence a lesser reduction requirement in the furnace. The Port Pirie double tuyere row design is a complicating factor avoided in both the Lumsden and Zhao prototype models by using idealised, stratified temperature/composition profiles in a presumed single tuyere row configuration. It must be acknowledged, however, that the Chimkent experiments were not intended to produce a simulation of larger-scale lead blast furnace operation, so much as to give confirmation of the relative effects of different levels of preheated blast, oxygen enrichment and the potential use of natural gas as a supplementary fuel. Each experimental run was started and continued only to the point of steady operation over a few hours, which allowed consistent and comparable measurements to be made. In contrast, an industrial-scale furnace takes several days after blowing-in before stable operation is achieved and then maintained for many months. Zhao's application of kinetic data from the Chimkent papers claiming similarity of the pilot-scale experiments to the Port Pirie industrial-scale furnace operation is simply not valid. Even Polyvyannyi states that there was only qualitative agreement between laboratory experiments and pilot-scale reaction sequences. Zhao, as with Polyvyannyi, fails to take into account any influence of volatilised zinc, either chemically or thermally.

Further light on the question of possible direct reduction is afforded by experiments with the aim of improving the performance of the commercial-scale lead blast furnace at

Brunswick Mining and Smelting Co, Belledune, Canada. The furnace configuration was that of a modified ISF using two double bells for charging. Compared with the Port Pirie furnace, the absence of a charging and gas offtake superstructure facilitated access for the introduction of sampling probes directly through the roof of the furnace. Separate experimental campaigns are described in the literature.

The initial campaign was limited to determining vertical gas composition, temperature and pressure profiles (Chao *et al*, 1978) during two separate periods, four months apart, at a single centre-line sampling point. Temperature variability with time was established by fixing probes at specific levels over ranges from 0.5 to three hours. Results of time-averaged temperature measurements and gas analyses were considered to show consistency between the two separate periods. Large temperature fluctuations (standard deviation (SD) >100°C) were noted near the stockline, reducing at depth (SD ~60°C). The paper reports periodic high-temperature excursions of the gas above the stockline, attributed to the combustion of CO with dilution air, although Port Pirie experience would suggest that this was more probably due to the hot-top behaviour of lead blast furnaces traditionally encountered in practice. The reported decision to delete all results of such perceived 'abnormal operation' is therefore questionable. In general, CO_2/CO ratios were much lower than those inferred by the Lumsden model for Port Pirie operation, but probably not surprisingly so given the high mass ratio of coke to sinter reported in the paper (double that used at Port Pirie). A provisional model of the blast furnace operation at Belledune was described in the paper, incorporating a zonal model based on the thermodynamic concept of chemical potential of the gases and using the CO_2/CO ratios measured in the field.

A specific criticism that can be made of this model – indeed, of all models cited in the present work except that of Lumsden – is a failure to appreciate the role of zinc cycling in the chemistry of lead sinter reduction and its effect on the validity of furnace gas samples. Only Chao *et al* (1978) mention the likelihood of significant zinc concentrations in the gas about 1.8 m above the tuyeres. Here the equilibrium Zn vapour partial pressure corresponding to the measured CO_2/CO ratio was calculated at 0.3 to 0.7 atm, assuming the ZnO activity to be 1 as a result of deposition of solid ZnO via the temperature reversion reaction. Accepting the probability of a solution of such deposited zinc oxide in the molten phase, and using the zinc content of the sinter feed and output slag as a guide, a more likely a_{ZnO} can be estimated as 0.3, so that the partial pressure of Zn corresponding to the measured CO_2/CO ratio should be 0.1 to 0.23 – about double Lumsden's calculated value for Port Pirie based on a much higher oxygen potential, but also higher a_{ZnO}, and assuming an equilibrium between gas and slag in the near-tuyere slagging zone. Moreover, the calculation by Chao *et al* does not allow for the fact that the gas sample from this level of the furnace would itself have contained Zn vapour. This would have reverted to oxide as it cooled en route to the measuring device, decreasing the CO_2 content and raising the CO content, resulting in a spuriously low measure of the apparent oxygen partial pressure. This is an inherent and experimentally insuperable problem in all gas analysis investigation into systems involving zinc reduction, including the ISF and slag fuming processes, but not the iron blast furnace process on whose modelling much of the published lead furnace modelling is based. Chao *et al* obviously disbelieved their calculated Zn partial pressures and took no further account of zinc reduction, but still estimated oxygen partial pressures from the spurious gas analyses. Polyvyannyi (1976) does mention that observed increases in total zinc content in charge samples and furnace accretions from this temperature zone were probably due to zinc recycling, but also fails to appreciate the associated effects on the heat balance of the zone, or any effect on the validity of gas analyses.

A later paper by Chao (1981) developed a dynamic model to simulate the operation of both the Belledune furnace and that operated by Cominco at Trail, British Columbia, Canada. The assumptions involved were extensive, but afforded a mathematical solution to the complex heat and mass transfer processes without considering the real influence of chemical kinetics – in essence an approach somewhat similar to that used by Lumsden at Port Pirie.

In a second Belledune experimental campaign (Morris *et al*, 1983), modified probes were used in which a recoverable cage packed with sinter was attached to the water-cooled temperature/gas sampling probe. The gas sampling thimble was located within the cage at its midpoint. Temperatures and pressures were measured as the probe descended with the charge while gas samples were preserved for subsequent analysis. The probe was withdrawn after reaching a predetermined depth. The recovered sinter sample was subjected to various analyses to determine its overall chemical constitution, mineral structure, phase makeup and degree of reduction.

Compared with the earlier experiments, the placement of the thermocouple and gas sampling points within the sinter mass in the cage recorded significantly lower temperatures, possibly reflecting a difference between solids temperature and the gas temperature measured previously. The temperature and gas probes failed through destruction and blockage respectively at levels below 2 m above the tuyeres. Gas analyses were scattered but generally within the ranges found earlier. The suite of analytical methods resulted in certain differences from the Chimkent work in the reporting of phase distributions. Chimkent used infrared spectroscopy to arrive at a quantitative analysis in mass per cent of the phases present; the Belledune experiments used scanning electron microscopy, with phase compositions reported as volume per cent. It is therefore not possible to produce a graph of lead speciation by mass against height above tuyere level as in Figure 6.

Together with descriptions of the sample cage contents, the data presented in Table 2 allow certain conclusions to be drawn that can be compared with the Chimkent pilot plant experience:

TABLE 2

Charge sample analysis, Belledune Smelter (Morris *et al*, 1983).

Height above tuyeres (m)	(Sinter feed)	4.45	3.35	3.05	2.74	2.68	2.44	2.01	1.28	1.13
Phase analysis (volume %)										
Pb silicates	39	43	47	40	43	41	19	24	4	1
Pb ferrite	7	7	1	1	0.5	0.1	<0.1	<0.01	nd	nd
Galena	tr	tr	tr	tr	tr	0.5	1	5	1	15
Pb metal	3	0.1	3	1	6	6	22	5	12	17
Zn ferrite + wüstite	35	38	30	38	37	38	34	33	31	18
Hardystonite ($Ca_2ZnSi_2O_7$)	16	12	20	20	14	15	24	33	52	44
Inferred solids temperature (°C)		300	700	780	850	850	900	1050	1120	1150
Elemental analysis (weight %)										
Pb^{II}	27.7	23.8	22.1	26.0	25.6	27.6	22.1	20.4	3.54	
Pb^0	2.64	5.28	7.36	4.91	4.58	2.56	8.55	9.97	11.2	
Fe^{III}	15.0	16.0	15.2	15.5	16.5	9.10	11.9	9.68	1.91	
Fe^{II}	6.5	6.8	7.0	6.3	5.6	12.8	9.4	10.8	25.9	18.3

nd – not determined; tr – trace.

- In both studies, all lead ferrite was substantially reduced in the upper furnace at temperatures below 800°C.
- The main silicate phase in the Belledune sinter at all levels was identified as a compound silicate, specifically $Pb_3Ca_2Si_3O_{11}$. No free PbO was reported in any of the samples. This contrasts with the Chimkent reports of the major phase in their work being lead silicate glasses based on Pb_2SiO_4, with significant amounts of lead ferrite and free PbO.
- In both studies there was virtually no reduction of lead silicates below 700°C. All reduction of the silicates must have taken place from the liquid state in the temperature range 780–1150°C.
- Certain experimental difficulties were encountered, particularly in retrieving samples from levels within 2 m of the tuyere level. Only a small amount of remnant material was left adhering to the cage structure, leading to a conclusion that the main fusion processes and phase separation occurred below the 2 m level. The phase analysis of material from this zone presented in Table 2 refers to the remnant material rather than bulk material in the sample cage, which was assumed to be backfill accumulated during withdrawal of the cage. Both the phase and chemical analyses of the remnant material show anomalous levels of metallic lead and galena relative to the input sinter, referred to in the text but otherwise not explained. The phase analyses revealed almost complete reduction of the lead-bearing silicates. Residual structures mainly comprised the high-melting components – zinc ferrite, wüstite and the melilite, hardystonite – in proportions approximating those present in the sinter as charged to the furnace.
- In contrast, a significant proportion of the lead silicate glasses in the Chimkent samples remained to be reduced at the 2 m level. Gas temperatures in the pilot furnace, however, were significantly lower than those in the production furnace at Belledune at this level, while solids temperatures were not determined. Samples for analysis were derived from bulked cross-sections of the furnace burden at 0.5 m vertical intervals compared with spot samples from different vertical levels but fixed horizontal coordinates. The differences in the experimental techniques appear to be such that the demonstrated differences in outcomes are hardly surprising. Nevertheless, the significance of the kinetics of liquid-phase lead silicate reduction is clear in both sets of results.
- The technique used in the Belledune experiments ensured there could be no direct contact between coke and sinter samples. All reduction in the samples was therefore by reaction with gaseous CO. The rate of the reduction reaction was sufficient for complete silicate reduction within the available residence time in the furnace. It was concluded that nearly all reduction reactions occurred in the zone 1–2 m above the tuyeres. Such a finding contrasts with the 1971 Chimkent postulate that most of the silicate reduction was by direct reaction with coke in the tuyere zone itself.
- Morris *et al* (1983) concluded that their findings in this study invalidated the model used by Chao (1981), but pointed to a lack of kinetic data in Western technical literature of the time relating to the reduction of lead silicates in the temperature range 800–1200°C.
- Both Belledune (Hussain and Morris, 1986) and Chimkent (Polyvyannyi, 1976) proceeded to laboratory studies of the kinetics of lead reduction from PbO and the principal lead-bearing phases observed in their respective industrial and pilot-scale experiences – in the one case $Pb_3Ca_2Si_3O_{11}$, in the other Pb_2SiO_4 and lead ferrite. The kinetics of reducing ground and pelletised sinter samples were also examined in each case.

Hussain and Morris (1986) showed that a grain model could be used to describe the laboratory outcomes of the reduction of solid-state sintered hematite, lead oxide and lead calcium silicate pellets by CO_2/CO gas mixtures. Kinetic parameters were established for the major reducible constituents of the Belledune sinter and also for measured changes in pore structure and surface areas as reduction proceeded. Similarly to experiments described in Polyvyannyi (1976), at temperatures between 835°C and 853°C reaction rates initially slowed following the transition of lead-bearing compounds from solid into liquid state, later followed by a rapid increase in reduction rate with increasing temperature. The model was successfully applied to the results of reduction experiments up to 1000°C on both pelletised ground sinter and pellets cut from as-received commercial sinter. Hussain and Morris concluded that the model qualitatively explained the reduction behaviour of sinter in the Belledune blast furnace.

It is suggested that the Belledune findings are not altogether inconsistent with Lumsden's concept of a furnace reaction zone in the temperature range 1000°C to 1150°C, initially for the case where all reduction of PbO had taken place above this zone, but later extended to a case where PbO reduction persisted until a temperature of 1060°C was reached. Lumsden's aim was to show the heat balance implications of exothermic reduction reactions with respect to the relativity of gas and charge temperatures. The oversimplification of reduction kinetics was clearly in error in light of the Belledune and Chimkent experiments, but the thermodynamic reasoning is not invalidated and the heat balance may still be capable of recalculation with more realistic kinetic data.

A problem remains, however, with the clearly apparent differences in the major reduction mechanisms revealed in the Chimkent and Belledune investigations. It is suggested that the mineralogy of the sinters is a significant factor, as will now be explored.

Sinter mineralogy and reduction kinetics

In general, the term 'sinter' implies a coherent mass of required strength and/or porosity produced from a powder by partial fusion using heat supplied by internal combustion processes or from external sources. In metal-forming and ceramic processing, sintered products of the required properties are produced from powders well below the melting points of single-component or simple mixtures with only a few components. In high-temperature extractive metallurgy, however, sintering is used as a means of producing an agglomerated, massive oxide product as an appropriate raw material for feeding to carbothermic reduction furnaces. The fluxes required for the phase separation of product metal and a slag containing collected impurities are included in the fusible powder mix.

In ferrous sintering practice, the constituent iron ore and flux materials are fused to make a single porous mass with little change in the chemical properties of the ingredients.

In the non-ferrous industries, and in particular the lead/zinc branches, the input ore powders to be sintered comprise a majority of sulfidic concentrates together with ancillary process recycles and fluxes. The aim of the sintering process is twofold: to achieve an appropriate degree of desulfurisation, and produce the massive fused product required for feeding the blast furnace. The exothermic reactions required for desulfurisation provide the necessary thermal energy for the fusion. The thermodynamic interactions occurring in achieving both aims in a single operation are complex, but at this point it is sufficient to say that adequate desulfurisation in the sintering process requires temperatures in excess of the fusion temperatures of most or all components in the combined sinter-reaction product.

The desulfurisation chemistry is discussed in Section 9.

The speciation of the sinter product into high and low melting phases referred to in the section dealing with sinter-softening behaviour strongly suggests that, far from being a fusion of individual phases present in the input components, the whole sinter mass is formed from a molten slaggy state. This melt crystallises on cooling into the various components affecting the softening behaviour of sinter as it passes through the thermal gradient in the blast furnace. Such a concept differs from the traditional view expressed in many metallurgical courses and texts (eg Sinclair, 2009) that sinter consists only of partly fused mass. The implications of the phase chemistry are now discussed.

The references so far used to describe sinter reduction kinetics have argued from observing the field behaviour of furnace feed and partially reduced sinters, followed by laboratory studies of reduction kinetics of pure reducible compounds representing the major components identified. Confirmatory studies applying derived kinetic parameters to the reduction behaviour of industrial sinters have led to the attempted theoretical modelling of the lead blast furnace process. This progression resulted from a gradually improving knowledge of the constitution of lead sinters enabled by improved instrumentation technology over the second half of last century. The most recent studies, using electron microprobe analysis to examine individual mineral grains within the sinter, reveal a vastly more complex range of phase composition variation than derived using earlier techniques.

At Port Pirie, early studies of the solid phases present in updraught lead sinter were carried out by Manson (1958) using optical microscopy to identify and describe mineral groupings familiar from even earlier studies on Port Pirie blast furnace slags. Other than metallic lead and unaltered charge material, phase groupings are identified in Table 3.

Manson's paper reflects the Port Pirie paradigm of the time that the mineral composition of the sinter was of minor importance compared with the PbO/metallic lead ratio and density/physical strength characteristics, which were major determinants of blast furnace performance. To this writer's knowledge, no further microscopy studies of this nature were carried out in the Port Pirie laboratories.

BHAS staff paid two visits to the Chimkent lead plant in Kazakhstan (then part of the Soviet Union) in 1976 and 1978 as a result of industrial research exchange initiatives proposed by the Soviet and Australian governments. Reference to the use of oxygen enrichment, preheated blast and natural gas injection in sintering, blast furnace and slag fuming applications had been among several interesting developments briefly described in abstracts of Russian language technical literature. Following discussions, the BHAS party was presented with several technical publications on these subjects – some authored by Chimkent operators, others by a group based at the Process Metallurgy Institute of the Kazakh Academy of Sciences in Alma-Ata (now called Almaty). The works relating to blast furnace investigations have been cited earlier in the text, especially those by Polyvyannyi (1976). This latter work included a review of numerous investigations by other Soviet authors into the kinetics of oxidic lead compound reduction, of which the BHAS party was largely unaware. Polyvyannyi's own work in conjunction with Chimkent is of direct relevance to the present discussion.

TABLE 3

Port Pirie sinter mineralogy (Manson, 1958).

Groupings	Minerals	Typical formula	Comments
Lead oxide	Litharge	PbO	Patches, often surrounding metallic lead particles, grading into silicate matrix.
Lead oxide compounds	PbO and silicates		Yellow-green matrix comprising main part of the sinter bonding material.
Spinels and ferrites	Zinc ferrite, magnetite	$Me^{I}O.Me^{II}_2O_3$	Numerous, crystalline. Colours range from black of ferrites, through red-brown to various shades of green, to colourless. Often banded indicating variable composition.
Melilites	Not nominated	$MeO.2CaO.2SiO_2$	Some rough cubic structures, more often colourless patches with numerous inclusions.

Early investigations into sinter constitution, probably in the mid- to late-1960s, involved optical microscopy and X-ray diffraction to identify mineral species in Chimkent lead sinters, as seen in Table 4.

Industrial-scale investigation into blast preheating and oxygen enrichment on the lead furnaces had given promising results, but progressed into detailed laboratory experimentation on the kinetics of sinter reduction. Pilot-scale experiments followed in which the contents of the shaft of an operating pilot furnace were frozen by the injection of nitrogen, then sectioned and studied in order to follow the sequence of events as the sinter passed downwards in the shaft. Infrared spectrometry was used to differentiate the behaviour of different lead species in the pilot-scale furnace.

For the lead blast furnace at Belledune, the application of scanning electron microscopy in conjunction with X-ray diffraction provided much higher definition in the examination of sinters and their reduction reactions. Table 5 provides a more detailed description of the mineralogy of Belledune input sinter than Table 2, which describes changes in the mineralogical groups as reduction proceeds within the furnace.

TABLE 4

Chimkent sinter mineralogy (Polyvyannyi, 1976).

Groupings	Minerals	Typical formula	Comments
Metallic lead			1–7%, unevenly distributed.
Lead oxide	Litharge	PbO	Glassy earthy inclusions in pores and cracks.
Lead silicates	3 observable forms	$PbO.SiO_2$ $2PbO.SiO_2$ $4PbO.SiO_2$	2–10% in crystalline form. About 30% in form of amorphous glass in yellow-green matrix with refractive index 1.95–2.08 comprising main part of the sinter bonding material.
Spinels and ferrites	Zinc ferrite, magnetite	$Me^{I}O.Me^{II}{}_2O_3$	Comprise 17–23% of the sinter. Inconsistent in colour, magnetic properties and structure, probably accounted for by a minor proportion of zinc in the magnetite phase.
Melilites	Gehlenite ($MeO = Al_2O_3$) Åkermanite ($MeO = MgO$)	$MeO.2CaO.2SiO_2$	Significant quantities.
Fayalite		$2FeO.SiO_2$	Some.
Sulfides	Galena Sphalerite	PbS $(Zn,Fe)S$	1–3% PbS deriving from original charge, but also secondary sulfides of Pb, Zn and Cu.

TABLE 5

Belledune sinter mineralogy (Morris *et al*, 1983).

Groupings	Minerals	Typical formula	Comments
Lead oxide	Litharge	PbO	None reported.
Lead silicate		$Pb_3Ca_2Si_3O_{11}$ $2PbO.SiO_2$	Principal phase. Second most common. Lead silicates generally intergrown with other phases.
Ferrite	Zinc ferrite + wüstite Lead ferrite	$ZnO.Fe_2O_3+FeO$ $PbO.Fe_2O_3$	Cubic grains within the lead silicates. Prismatic grains.
Melilite	Hardystonite	$Ca_2ZnSi_2O_7$	Individual and clusters of prismatic grains.
Other silicates	Andradite	$Ca_3Fe_2Si_3O_{12}$	
Residual sulfur	Anglesite Lanarkite Anhydrite Galena	$PbSO_4$ $PbO.PbSO_4$ $CaSO_4$ PbS	

Notable differences from the earlier works were that the sinter in this case appeared to be completely devitrified (that is, no glassy phase reported); the principal phase was a compound confirmed by X-ray diffraction as being the lead calcium silicate $Pb_3Ca_2Si_3O_{11}$; and no free PbO was present. A comparison of the chemical composition of the three sinters (Table 6) provides an explanation for such differences.

The Belledune sinter shows an unusually high FeO/SiO_2 ratio together with moderately high CaO and low PbO values. A simple calculation shows that a mass balance between CaO, SiO_2 and PbO in the nominated silicate and melilite phases can only be achieved if all PbO is taken up in these phases; that is, free PbO cannot be formed. It should further be noted that when plotted on the ternary phase diagram $CaO\text{-}FeO\text{-}SiO_2$, a blast furnace slag formed from sinter with these CaO/SiO_2 and FeO/SiO_2 ratios would fall outside the range common to other lead smelters (Manson and Segnit, 1956; Winterhager and Kammel, 1961; Sinclair, 2009). This would suggest a high slag liquidus temperature of about 1200°C, which may have been the cause of the high coke consumption and furnace freezing problems noted by Chao *et al* (1978). Nevertheless, the reported differences in mineralogy and composition from the Chimkent and Port Pirie sinters raise the question as to whether the reduction kinetics of the Belledune sinter have general applicability.

A more general clarification of the mineralogy of lead blast furnace sinters is afforded by a later paper by van Huyssteen, Harris and Hancock (1992), who made over 400 electron microprobe analyses of seven production sinters from Belledune. Compositional variations in mineral groups were shown to be much more complex than suggested by earlier investigations. By examining elemental substitutions in the various mineral structures, the sequence in which various phases formed during sintering could be established. The relationship between the bulk chemistry of a given sinter and the speciation of elements in the observed phases could also be confirmed. Rather than many mineral groups of fixed stoichiometry being formed as implied in Table 4, it was shown that more general formulae should be used, allowing for various elemental substitutions to take place as the composition of the residual liquid matrix itself varies as a result of the precipitation of solid phases. A much abbreviated selective summary of the mineralogy of these groups is now given with respect to their general formulae rather than the specific compositions:

- *Hardystonite* $(Ca,Pb)_2(Zn,Mg)Si_2O_7$ – PbO content varied between 4.4 and 11.6 per cent inversely with the CaO content. Grains were regularly zoned, with PbO a minimum at the core of the grain to a maximum at its edge. MgO could substitute for ZnO in the hardystonite lattice. The displaced ZnO in the still molten matrix participated in reactions that consume silica and PbO to form observable amounts of larsenite ($PbZnSiO_4$), not mentioned in the previous publications.
- *Zinc spinel* $(Zn,Fe)O.(Fe,Al)_2O_3$ – pure $ZnFe_2O_4$ did not occur. The earliest spinels to form were those with MgO (1–4 per cent) and Al_2O_3 (1–4.5 per cent). Trivalent Al ions would displace ferric ions. MgO in the zinc spinel was highly correlated with MgO in the sinter feed, releasing other divalent species to react with and deplete Si in the matrix.

TABLE 6
Comparative chemical compositions of Port Pirie, Belledune and Chimkent sinters (w/w).

Site	Pb	SiO_2	FeO[a]	CaO	ZnO	Al_2O_3	MgO	S	Total	CaO/SiO_2	FeO/SiO_2
Port Pirie	50	10.0	12.4	6.1	10.7	2.7	1.1	1.9	94.7	0.60	1.24
Belledune	30.6	12.7	28.3	8.7	7.2			1.2	88.7	0.69	2.23
Chimkent	40.5	11.2	14.3	6.1	11.2	3.1	1.1	2.1	89.5	0.54	1.28

[a] All iron reported as FeO.

Inclusion of zinc spinel crystals within hardystonite grains indicated their formation prior to that of hardystonite.

- *Larsenite* ($PbZnSiO_4$) – suggested formation was a result of functionally lime-poor areas where insufficient lime was present to form hardystonite. Lime needed to be in the form of calcium silicate rather than anhydrite ($CaSO_4$). High concentrations of larsenite correlated with high MgO samples.
- *Ferrites* – ferrites were formed under partially reducing conditions that produced magnetite ($FeO.Fe_2O_3$) with a spinel structure formed much later than the zinc spinels.
- *Wüstite* (FeO) – was exsolved from lead calcium silicates formed at higher temperatures.
- *Galena* (PbS) – was common but of secondary origin rather than residual concentrate.
- *Anhydrite and other sulfates* – Ca-sulfates, Pb-Ca-sulfates and lanarkite (Pb_2SO_5) were detected in varying proportions, but all sinters contained sulfates at up to five per cent. Formation was suggested as due to the reaction of lime flux with S and Pb fumes.
- *Pb-silicates* – compositions were highly variable because they were the residue left after formation of other phases. The predominant Pb-silicate was $2PbO.SiO_2$ but with numerous substitutions, varying from low lime-iron-rich to high lime-iron-poor. The sequence of formation of the various mineral groups during formation and cooling of the sinter production melt at Belledune was shown to be: sulfates, Zn-spinels, hardystonite and other melilites, larsenite, Pb-Ca-arsenates, lead silicates, magnetic ferrites and metallic lead. The wide variations of possible compositional mineral groups demonstrated in this work, combined with lead smelting slags generally falling within a fairly narrow range of CaO/SiO_2 and FeO/SiO_2 ratios, suggest that this sequence would be valid for most lead sintering/blast furnace operations.

In the case of the exceptionally high ratio of lead to slag-forming constituents in the Port Pirie sinters used prior to the commencement of slag-fuming operations in 1967 (Table 5), it is quite probable that lead content in excess of stoichiometric mineral formation requirements would report as both metallic lead and PbO, as observed by Manson (1958).

In summary, the microprobe analyses of van Huyssteen, Harris and Hancock (1992) provide evidence that the Belledune lead sinters consisted of mineral group species, all of which varied systematically with respect to composition and melting point, rather than the specific compounds supposedly identified in previous studies by microscope and X-ray diffraction methods. These group species demonstrated the ability to substitute minor slag component species such as Al_2O_3, MgO, As_2O_3 into their structure. The presence of magnetic ferrites as products of slightly reducing conditions was also demonstrated. It is logical that such structural and compositional groupings should be the case in general for all self-fluxing lead blast furnace feed materials, given the restricted composition range of their product slags. However, such variability renders the laboratory evaluation, general interpretation and predictive modelling of the reduction behaviour of production sinters virtually impossible.

The behaviour of such heterogeneous sinter is now considered as it is heated and subjected to reduction while passing down the shaft of a lead blast furnace.

It is reasonable to assume that some initial reduction takes place in the solid state, specifically that of free lead oxide and non-zinc ferrites, at solids temperatures no higher than about 750–800°C. Both Polyvyannyi (1976) and Hussain and Morris (1986) conclude that such solid-state reductions by CO/CO_2 gas mixtures are limited by chemical rate control since gas molecules appear to be able to penetrate the porous sinter structure quite freely; that is, gaseous diffusion not being limiting. The lower energies of activation of these compounds relative to the silicates suggests that at these temperatures the reduction should be quite specific, as has been observed in practice. Porosity and consequent interfacial areas necessary to determine overall reaction kinetics were measured by Hussain and Morris using mercury porosimetry. Areas were in the same order of magnitude as those determined by the BET method by Ward (1959) on Port Pirie sinter. The reaction was also shown to be first order with respect to CO partial pressure. Laboratory data relating to the solid-state reduction of individual sintered compacts of PbO, Fe_2O_3 and $Pb_3Ca_2Si_3O_7$ were simulated by Hussain and Morris using a grain model. At 800°C (slightly above the melting point of PbO), the experimental PbO reduction rate was significantly lower than the model prediction, as also found by Polyvyannyi. The model failed to predict the reduction behaviour of synthetic commercial sinter consisting of a sintered mixture of hematite and lead calcium silicate. Laboratory experiments on the CO reduction of commercial sinter pellets were inconclusive because of the confounding effects of weight loss of the experimental samples due to (volatilisation) reactions other than reduction. Hussain and Morris's use of the grain model to extrapolate the effects of temperature, porosity and pellet diameter on the reduction of lead calcium silicate to lead smelting temperatures in excess of 1000°C is far from convincing, if only because the presumably high-melting stoichiometric compound $Pb_3Ca_2Si_3O_7$ was reported in only one of the Belledune investigations. Such a specific compound was not identified by van Huyssteen, Harris and Hancock (1992), although that paper noted the occurrence of residual lead silicates separately categorised as CaO-rich/Fe-poor and CaO-poor/Fe-rich. These studies would suggest that such residual lead silicates would be low-melting, but at temperatures above that of residual 'free' PbO, which is the final form of any excess oxidised lead that cannot be accommodated in higher melting compounds. It is concluded that the grain model is applicable only in the case of solid oxide reduction to produce a liquid product.

The kinetics of solid-state reduction by hydrogen and carbon monoxide of Chimkent charge samples from different levels down to tuyere level in the pilot furnace were examined in laboratory studies described by Polyvyannyi (1976). Finely ground samples were reduced by the pure gases at temperatures from 600°C to 1000°C. Kinetic data (rate constants and energies of activation) varied with both depth in the furnace and degree of reduction in the laboratory tests. Zhao (1993) applied these data to his attempted modelling of the Port Pirie furnace, claiming similarity with the Chimkent pilot operation. Such similarity has been shown not to be the case. It also seems unreasonable to consider that the lower-temperature solid-state laboratory reduction of finely ground samples taken from the tuyere zone after freezing the furnace could in any way replicate the actual conditions of high-temperature liquid-phase reduction during operation.

The discussion relating to Figure 6 indicates that in the Chimkent pilot-scale lead blast furnace experiments, the solid-state reduction of the 12 per cent of the lead present as free PbO in the input sinter was substantial, but some free PbO remained to be reduced above 800°C. All was consumed by the time the temperature reached 1000°C. All lead ferrite was reduced at temperatures below 800°C. No free PbO was reported in the Belledune input sinters, which had an unusually low total lead tenor in the earlier papers.

It can be concluded from the Chimkent and Belledune studies that the main part of reduction in the lead blast furnace takes place from compounds in the liquid state. The detailed analyses of solidified phases in Belledune input sinters by van Huyssteen, Harris and Hancock (1992) shows that although these phases can be grouped as mineral types, none can be regarded as pure compounds as all contain varying proportions of PbO and slag-forming oxides. It follows that as the matrix cools during the sintering process, the liquid phase remaining as a particular mineral group crystallises must also vary continuously in composition until the final solidification of the lowest melting silicates, non-zinc ferrites and any residual PbO. In the blast furnace, as the charge is heated beyond 800°C, the phases begin to melt in the reverse order, but now under more reducing conditions than during the sintering operation.

The mechanisms of reduction of the liquid, mainly silicate, phases are best described in terms of observed behaviour during the industrial-scale tests at Belledune (Morris *et al*, 1983) and the pilot trials at Chimkent (Polyvyannyi *et al*, 1971). Liquid-phase reduction kinetic data for the pure lead silicates $2PbO.SiO_2$ and $PbO.SiO_2$ tabulated in Polyvyannyi (1976) at temperatures up to 1200°C are not relevant in the context of the demonstrated complexity of real lead blast furnace melts. Similarly, kinetic data determined up to 1000°C for the laboratory reduction of finely ground charge samples taken from different levels in the Chimkent pilot furnace charge using pure hydrogen, carbon monoxide and carbon are of limited relevance, merely confirming rate dependence on lead silicate content, degree of lead reduction and temperature.

The liquid phases initially formed tend to fill the pore structure within still unreacted sinter so that the reaction now occurs at a limited gas/liquid interfacial area. According to both papers, reduction of the silicates became significant at a level of about 2.5 m above the tuyere axis. At this level Morris *et al* (1983) measured solid temperatures of 850–900°C while both Chao *et al* (1978) and Polyvyannyi *et al* (1971) measured gas temperatures at 1000°C. (These were probably consistent with the different gas and solid temperature profiles since each experimental method could measure only one – either gas or charge, but not both.) At this level Polyvyannyi *et al* (1971) reports some compaction of the sinter that retained a porous structure. At the 1 m level, both gas and charge temperatures could be assumed to be about the same at 1050°C. The charge had become heavily compacted, dense and of low porosity from the 2 m level downwards. The silicates were disappearing as lead was reduced. The ferric iron content of zinc ferrites was beginning to be reduced to wüstite (FeO), releasing zinc oxide to form additional hardystonite with free calcium oxide and silica (Morris *et al*). At 1.2 m the Belledune tests suggested temperatures of 1120–1150°C. Morris *et al* believed that the charge had become fully molten and had flowed out of the sample cage. The analysis of residual material adhering to the cage structure could be interpreted as that of slag containing metallic lead. In the Chimkent pilot furnace the gas temperature 0.5–0.7 m above the tuyeres was 1050–1100°C. In this range, the majority of the lead reduction took place, but 20–30 per cent of the lead remained unreduced. The earlier paper by Polyvyannyi *et al* (1971) claimed that at this level the slag content of the unreduced sinter had not fused and separated. Polyvyannyi (1976), however, stated that localised formation of the first slag-containing systems was observed in the solids from a zone corresponding to a gas temperature of 840°C. As the sinter moved downwards, the appearance of liquid phases, rate of slag formation and final slag production increased to completion in the tuyere zone. The majority of the remaining oxide lead was considered to be reduced from the liquid state in the tuyere zone at 1180–1270°C, with some phase separation of slag and bullion taking place there and below the tuyeres.

Considering all the information at hand, the following may be concluded with respect to influences on the reduction of molten phases in the furnace shaft above the equilibrium zone:

- Gaseous reduction takes place at the liquid surface of high lead content (that is, low melting point) silicates commencing in the 850–900°C range, with rates of reduction increasing rapidly as the temperature rises.
- As the sinter descends in the furnace, the oxidised lead content of the liquid phase decreases, both as a result of reduction and from the melting of silicates and other compounds containing only a minor proportion of lead. The residual silica-rich melt absorbs slag-forming charge constituents to maintain a molten phase within the

supporting lattice structure of high-melting phases of the original sinter. Some metallic lead product is maintained within the structure. How the interfacial reaction area of the residual liquid might alter under these conditions would appear to be undefinable.

- The softening and melting of sinter components as the temperature rises is not an exact reversal of the sequence of cooling processes occurring during the sintering operation. As heating in the blast furnace occurs under reducing conditions, the lead content (and hence PbO activity) of the molten phase changes, both as a result of the reduction of lead oxide species as well as the fusion of higher-melting species. It is not logical to consider the kinetics of melt reduction as that of a mixture of individual pure species with reduction kinetics extrapolated from lower-temperature solid-state reduction experiments.
- At some point in the temperature gradient, the supporting lattice structure breaks down and dissolves in the incipient slag melt so that slag and metallic lead product are free to run through and over the carbon bed. A reduction situation is now set up, similar to that occurring in the coke bed of the Kivcet process as discussed earlier, the main difference being the limited reaction surface with the large lumps of residual coke observed in this area of the furnace by Polyvyannyi *et al* (1971). The experiments by Morris *et al* (1983) summarised in Table 2 suggest this takes place at a temperature somewhat above 1050°C, which is consistent with the lowest temperatures for feasible slag viscosity measurements made by Winterhager and Kammel (1961) on over 30 industrial slags from different lead smelters.

Despite the complex and confusing reduction behaviour of the oxidised lead-bearing charge materials in the lead blast furnace, there is nothing to suggest that chemical or diffusion rates that control reduction reactions are directly limiting on overall furnace productivity. Even in the case of the short residence time available for reduction in the Chimkent pilot-scale furnace, the lead content in discharge slag was within the traditionally acceptable range, albeit with significant reduction in the tuyere and subtuyere zones. Industrial experience supported by statistical studies consistently shows that the limitation on throughput rates is determined by the blast air rate. The blast rate is determined largely by the charge permeability, which is affected by the relative size ranges of the sinter and coke components and potential compaction – through softening – of the sinter charge. It is also partly limited by the tendency of high-temperature reaction zones to rise upwards in the furnace, breaking through the upper surface of the charge in the phenomenon of 'hot top' with its unacceptable economic, industrial hygiene and environmental connotations. It is by the intensity and location of exothermic reactions within the furnace column, resulting in physical constraints on throughput rates, that chemical kinetics and their modelling remain important in the overall furnace chemistry.

To this extent, Lumsden's conception of the limiting influences on lead blast furnace operation was correct, but his assumptions as to the defining kinetic mechanisms were not.

The zonal reduction profile of the lead blast furnace

On the experimental evidence discussed in Sections 6, 7 and 8, it is postulated that the furnace charge column can now be envisaged as three contingent and possibly overlapping zones characterised by the physical state of the non-coke fraction. From the stockline downwards:

A. *The upper reduction zone* – a solid-state zone in which all reduction takes place by chemically controlled reaction between the gas phase and the solid oxide phases PbO and lead ferrite. The reduction gas is able to penetrate the solids that exhibit increasing porosity as reaction proceeds. Zinc vapour contained in the gas rising from below reverts to zinc oxide prior to exit from the charge column. The descending charge is heated physically by the counter-current gases, exothermic reduction reactions and zinc vapour reversion.

B. *The lower reduction zone* – a mixed-mode heat-and-mass-transfer zone characterised at lower temperatures by the reduction of molten lead-bearing silicates supported within a lattice-like structure of high-melting melilites and spinels; at higher temperatures coke starts to be consumed by gasification reaction with CO_2, while liquid-phase reduction continues and slag formation commences. As the temperature rises, the melting of liquid lead-based silicate glasses firstly causes the gradual softening of the sinter, resulting in compaction but with substantial retention of its structure. At higher temperatures lattice components also begin to melt into the liquid phase, gradually forming a free-running slag at a temperature tending towards that in the underlying equilibrium zone. Reduction is achieved by chemically controlled reactions between the liquid silicate phases and CO and Zn vapour in the gas phase. Heating of the charge is mainly by exothermic reduction reactions and zinc reversion counterbalanced by endothermic carbon gasification (by reaction with CO_2 to form CO) and slag formation. The reduction of lead compounds may effectively cease within this zone. Below this point, gas and slag are at equilibrium, but rate-controlling carbon gasification of the coke fraction continues while thermal balance is maintained by reversion of volatiles from the rising gas phase.

C. *The equilibrium zone* – encompasses a slagging zone comprising tuyere (coke combustion by air injection) and phase-separation functions. The slag is fully formed and in equilibrium with the gas and bullion phases. Phase separation of bullion from slag takes place to a substantial extent but not to completion.

Such a division retains the Lumsden concept of a thermochemical equilibrium that explains the consistency of the outcomes of smelting, both within and between operating sites, in respect of product temperatures and compositions. It allows for the known physico-chemical limitations and vagaries of the carbothermic reduction process in the column of a lead blast furnace. It retains Lumsden's assessment of the overall thermal significance of the exothermic nature of the input oxide species reduction, but now requires a better definition of overlapping rate control mechanisms dictated by physical phase changes within the charge.

Before discussing the possibility of modelling such a system, it is first necessary to consider the deportment of the sulfur component of the charge, which is thermochemically, physically and economically important in commercial lead blast furnace operation.

9

Sulfur Deportment in the Lead Blast Furnace

The Lumsden (1960) model of lead blast furnace chemistry had little to say about any major influence of sulfur deportment other than its effect on zonal and overall heat balances. The volatilisation of PbS in the slagging zone and its subsequent condensation and recirculation was certainly a factor in equilibrium and lower-reaction zone heat balance considerations, but this had no net effect on the overall furnace heat balance. Otherwise, the removal of sulfur from the furnace was assumed to be as SO_2 from sulfates by a general but unspecified mechanism whose endothermic effect was assumed to take place at a temperature somewhere below 1000°C. Its thermal contribution was recognised in the overall heat balance as a constant penalty per mole of PbO reduced in the upper reduction zones. Subsequent developments at Port Pirie in copper by-product recovery and battery scrap treatment were to result in much closer attention to both thermal and chemical implications of sulfur deportment on both blast furnace and ancillary process performance.

The lead blast furnace has only a limited capacity for eliminating sulfur entering in various forms within its feed materials. SO_2 and suspended sulfur-bearing particulates are removed in the exit gases; the balance reports in the molten products of the blast furnace process – dissolved or suspended in bullion, slag and in special applications in a copper-rich matte. When this capacity is exceeded, high-melting sulfidic materials usually rich in zinc accumulate as accretions in various locations within the furnace, limiting production rates and eventually requiring the termination of the operating campaign for a clean-out of the shaft and hearth. Zinc sulfide was very early identified as a deleterious component in feed materials high in both zinc and sulfur contents (Hofman, 1899; Iles, 1902). It is probable that the survival of the lead blast furnace as the major method of producing metallic lead from sulfidic materials was guaranteed only by two important metallurgical developments in the early decades of the last century. These were froth flotation as a means of concentrating and separating individual metallic sulfide minerals, followed soon afterwards by the development of the sintering machine as a method of desulfurising and agglomerating the finely divided lead sulfide concentrate product into the strong lumpy form resembling the oxidic ores – the traditional but declining source of blast furnace feed.

Hofman's account of blast furnace chemistry recognised that a minor amount of zinc contained in the sinter feed to the blast furnace could be coped with, providing that the sulfur content could be kept to a minimum. The downdraught sintering process evolved into a two-stage process with this end in view. Even so, the extensive investigations into North American lead sintering and blast furnace practice during the 1920s and early 1930s by Oldright and Miller (1936) still showed the accumulation of zinc sulfide in wall accretions and, more importantly, as accretions between the bullion and slag layer in the furnace crucible, which eventually led to the fatal closure of the connection of bullion flow to the lead well discharge. Ruddle (1957) revisited Oldright and Miller's work in light of subsequent developments in sintering and blast furnace practice. While noting improvements in blast furnace performance, particularly the effect of increasing furnace widths in reducing the effects of wall accretions as at Port Pirie, Ruddle was pessimistic about the possibility of further modifying the process chemistry by lowering sinter sulfur content or by using some (unidentified) fluxing agent. His major conclusion was that further improvement in operational performance could only come through changes in furnace design.

At Port Pirie, blast furnace operations since 1921 had been very much influenced by the expectation that the recovery of zinc from lead blast furnace slags would eventually become technically and economically feasible. Following pre-WWI work at the original Sulphide Corporation at Cockle Creek, a review by Courtney (1920) had concluded that the pyrometallurgical recovery of zinc by carbon reduction either in a shaft or a reverberatory furnace was technically feasible, but that economic recovery required high concentrations of zinc in the feed materials. These conclusions later came to fruition with the development of the ISF and slag-fuming processes. In anticipation of such processes, a consequence at Port Pirie was a series of experiments to establish operating practices to achieve the highest concentration of zinc in slag that could be tolerated in the lead blast furnaces there – about 18 per cent (Green, 1977). Such a high figure demanded rigorous control of sulfur in the furnace feed, and research emphasis was placed on the efficacy and consistency of sulfur elimination during sintering. This resulted in a two-stage downdraught process of increasing unit size, the development of which continued until 1955 when it was replaced by single-stage updraught sintering. With this new technique sulfur elimination was no longer a serious issue (Hopkins, 1958). Research emphasis subsequently changed to control of the physical structure and degree of oxidation of the sinter product, both factors of which were deemed important in the productivity of the blast furnace.

The major modification of Port Pirie blast furnace practice in 1964 – involving the elimination of the crucible, a new design of the hearth and subtuyere zone, combined with continuous tapping of both bullion and slag through the same outlet – led to significant improvement in furnace productivity and operating life (Fern and Jones, 1975). Outcomes among others attributable to the modifications were a steadiness of hearth operations, and a higher temperature of the product slag and (especially) lead bullion. The intended significant reduction in previous operating difficulties related to accretions in the crucible was achieved. While the development was essentially a practical evolution based on observation and operation, the fact that molten products leave the furnace through the one exit (arguably in a state of chemical and thermal equilibrium) permits some elucidation of the thermochemistry of volatilisation and accretion-forming mechanisms in the hearth zone of the furnace.

Thermochemistry of sulfur deportment in the hearth zone

Lumsden (1960) showed that an assumption of an equilibrium zone towards the hearth zone of the pre-1964 furnace necessarily involved volatilisation of PbS(g) and Zn(g) species into the gas phase while limiting the equilibrium temperature of the reaction products to about 1150°C, in line with observed furnace behaviour. Reactions occurring in this zone leading to the volatilisation of lead sulfide and zinc could be summarised in the equilibrium reaction:

$$\mathrm{Pb(l)} + \mathrm{ZnS(s)(slag, bullion)} \rightleftharpoons \mathrm{PbS(g)} + \mathrm{Zn(g)} \tag{9.1}$$

by which the partial pressures of the gaseous species were related in terms of the activity of zinc sulfide in the bullion and slag phases:

$$K = \frac{p\mathrm{PbS(g)} * p\mathrm{Zn(g)}}{a\mathrm{ZnS(s)}} \tag{9.2}$$

In that lead sulfide and zinc vapour were formed independently, Lumsden preferred to use the equilibrium relationships for the reactions:

$$\mathrm{ZnS(s)(slag) + Pb(l) + CO_2(g) \rightleftharpoons ZnO(s)(slag) + PbS(g) + CO(g)} \tag{9.3}$$

and

$$\mathrm{ZnO(s)(slag) + CO(g) \rightleftharpoons Zn(g) + CO_2(g)} \tag{9.4}$$

to show that the equilibrium values for the partial pressures of Zn(g) and PbS (g) were also determined by the CO_2/CO ratio (effectively, by the oxygen potential) and the activities of both ZnO and ZnS in the slag phase. Lumsden used estimated values of 0.82 and 0.62 for $aZnO$ and $aZnS$ respectively (without explaining how this was done) to calculate the partial pressures of zinc and lead sulfide for a range of CO_2/CO ratios from 2.5 to 5 at 1150°C. From considering the heat balance of the blast furnace hearth zone, Lumsden concluded that the most likely value of the CO_2/CO ratio for the blast furnaces of the time was about 4. Subsequent recalculations using more up-to-date thermodynamic data suggest a value of 3 might have been more appropriate.

Several studies have since provided empirical formulae for better estimating oxide activities in slags. The general applicability of such models has been discussed by Hollitt (1992). Sufficient data on lead slags have been accumulated to allow confidence in predicting the activities of oxide components of interest. The oxygen potentials of lead slags (and hence PbO activities) have also been measured directly, both in the laboratory and in the field using solid electrolyte probes (Hollitt, 1984a; Fontainas, Verhulst and Bruwier, 1985).

The calculation of sulfide activities in slags, however, has presented certain conceptual difficulties. Individual sulfides are not present as identifiable dissolved species but have thermodynamic activities arising from the shared interaction of metallic cation species with both sulfur and oxygen anions (Willis, 1980; Hollitt, 1992). Nevertheless, some success in the empirical estimation of sulfide activities from slag compositions has been reported by Pelton, Eriksson and Romero-Serrano (1993). A perhaps more rigorous method of estimating sulfide activities in the lead blast furnace hearth equilibrium system is by calculating the sulfur pressure of the equilibrium gas phase from the sulfur dissolved in the bullion phase. Willis (1980), however, had noted a disparity in experimental results between PbS solubility in lead calculated from H_2S/H_2 ratios and that measured directly, suggesting further work was needed on dilute solutions of sulfur in lead. Rytkönen, Pelro and Taskinen (1986) later showed that the discrepancy could be resolved by making allowance for concentration effects on the activity coefficient of sulfur in lead by using a self-interaction coefficient for sulfur in lead. By applying such modification to the formula derived by Grant and Russell (1970), their results can be shown to conform with direct high-temperature measurements of several authors to describe the behaviour of PbS in solution in lead. The regular solution model developed by Schuhmann *et al* (1976) appears to fail at low concentrations of S, such as those in the Port Pirie bullion, for reasons discussed by Willis.

In the Port Pirie lead furnace, approximate hourly measurements showed that over a period of 12 days during 1973, the bullion contained 0.3–0.4 per cent S and about 1.0 per cent

Cu at a mean temperature of 1164°C with a standard deviation of ±12°C (Barnett, 1976). The maximum measured temperature was 1220°C and the minimum 1120°C. By applying the Rytkönen, Pelro and Taskinen (1986) modification of Grant and Russell's formula, the sulfur pressure of such bullion at 1200°C can be calculated to be $2.04–3.51 \cdot 10^{-5}$ atm. At 1150°C the corresponding figures are $1.12–1.93 \cdot 10^{-5}$ atm. Hollitt (1984a) measured the equilibrium oxygen partial pressure of a typical Port Pirie slag at 1200°C as $9.87 \cdot 10^{-11}$ atm, which converts to a corresponding figure of $2.22 \cdot 10^{-11}$ atm at 1150°C. The activities of ZnO(s) for the Port Pirie slag used by Hollitt were calculated as 0.58 (1200°C) and 0.67 (1150°C). From these data, the activity of ZnS(s) is estimated to have been 0.78–1.02 at 1150°C and 0.55–0.72 at 1200°C.

These calculations suggest that the system would have become saturated with respect to zinc sulfide at the lower operating temperatures and at higher bullion sulfur concentrations. The higher concentrations were derived from matte analyses and production mass balances for sulfur in the subsequent copper drossing process. These data were considered a more correct estimate for the bullion analysis (Barnett, 1976) than the routine analyses of field samples. The lower sulfur values from chemical analyses of bullion samples were shown to be about 40 per cent below the production mass balance figures, possibly because of phase separation in the sampling ladle.

The conclusion to be drawn from the calculated ZnS(s) activity figures is that, under average operating conditions of the post-1964 modification of the Port Pirie furnace, there should be no precipitation of ZnS in the hearth zone. Nevertheless, given the temperature fluctuations occurring during furnace operations as indicated, it is inevitable some general precipitation of a high-melting solid ZnS phase could occur from time to time and from place to place within the furnace because of variations in the charge/coke/blast air mass balance over the area of the furnace. Operating experience suggests that this could be the cause of the formation of a refractory ZnS-rich layer between the separate bullion and slag phases within the furnace. This had been a particular problem in earlier furnaces where the deep crucible/siphon configuration meant the bullion exit temperature was consistently 100–150°C lower than that of the slag. Maintaining the internal connection of the flow of lead to the siphon was always a major source of operating problems, often giving rise to the use of explosives to break up accretions. Oldright and Miller (1936) had also shown that accretions forming at the bullion and slag interface that were trapped in place by the underflow weir of the lead siphon in such furnaces consisted mainly of zinc sulfide. In contrast, besides higher bullion exit temperatures, one of the major operating advantages of the newer continuous-tapping configuration was that the tapping outlet level was at the slag/bullion interface so that any solid precipitates tended to be removed together with the products. Practical confirmation of the tendency towards ZnS precipitation through cooling was afforded during early stages of developing the continuous tapper by the formation of serious sulfidic accretions near regions of constricted slag and bullion flow, and hence lower temperatures at the water-jacketed outlet. This problem was solved through enlargement and improvements in the design of the outlet. The Fern and Jones (1975) paper illustrates the 'bay window' design of the eventual successful configuration.

It is pointed out that these arguments apply to the particular case of the high zinc slags used at Port Pirie. For other locations, furnace configurations, temperature regimes and mass and energy balances, quite different sulfur potentials and ZnS activities may apply, but the problem of sulfidic accretions seems to have been quite general. Given the bullion temperature regimes cited by Oldright and Miller (1936), it would seem likely that the severe hearth accretion problems caused by ZnS deposition were due to the mechanism described.

Regarding side-wall accretions, a revision of Lumsden's calculation of the gas phase composition at 1150°C in the equilibrium zone of the furnace indicates partial pressures of Zn and PbS vapours of 0.058 and 0.014 atm respectively, at a CO_2/CO ratio of 3:1. As this gas rises through the furnace, it is subject to both vertical and horizontal thermal gradients, in each case because of differences in temperature between the gases and charge materials. The horizontal gradients arise mainly through the cooling effect of the water-jacketed walls, but also as a result of the physical change of direction of the blast from horizontal at the tuyeres to vertical as it passes upwards towards discharge from the surface of the charge column. Accordingly, the horizontal gradients lead to solid accretions at the walls and in the centre of the furnace column. The vertical temperature gradients arise from heat transfer from the rising gases to raise the temperature of the descending charge. The thermochemistry of the gas system when subjected to a falling temperature requires the strongly exothermic reversion of the reactions in Equations 9.3 and 9.4:

$$\mathrm{Zn(g) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)}$$

and

$$\mathrm{ZnO(s) + PbS(g) + CO(g) \rightleftharpoons ZnS(s) + Pb(l) + CO_2(g)}$$

with formation of solid ZnO and ZnS and consequent changes to the CO_2/CO ratio. Examination of the thermochemistry of the gas system shows that all PbS vapour should be effectively converted to solid ZnS by the time the gas temperature is lowered to 1000°C.

The question arises as to whether the ZnS might form as a fume suspended in the rising gases or whether reversion should effectively take place at the lowest temperature in the gradient (at the interface between gas and charge). Operational data (although from different times) suggests that of an estimated 0.02 g S volatilised as PbS in the equilibrium zone per gram of product bullion (Lumsden, 1960), only 0.0014 g S carries into fume in the exit gases (Barnett, 1976). While there were certainly differences in operating parameters between the two sets of data, these would not have been sufficient to render the comparison invalid. It is therefore concluded that the contribution of reversion reactions to the sulfur content of fume in the exit gases is minor, and that reversion effectively takes place at the gas/charge interface, thus providing the important mechanism for heat transfer from gas to solids envisaged in Lumsden's model.

Such a mechanism requires that the ZnS forms as a deposit on the charge with a simultaneous release of the reaction heat directly to the charge. This scenario suggests that sulfur should then form a cyclic load within the burden being volatilised as PbS at the higher equilibrium zone temperatures, condensing on the charge at lower temperatures and returning within the charge as ZnS. In practice, the horizontal temperature gradient imposed by the water-jacketed furnace walls should also result in ZnS enrichment of accretions low in the furnace, as has been recorded in the literature (Oldright and Miller, 1936; Ruddle, 1957; Polyvyannyi *et al*, 1971). Operating problems arising from side-wall accretion formation were reduced substantially at Port Pirie during the period 1935–1947 with the development of wide furnaces with two rows of tuyeres at different levels (Green, 1977). No experimental work into such accretion formation and composition was carried out by the Research Department in this writer's experience from 1956 onwards. Operating experience was certainly that accretions (locally termed 'banks') did form on the lower walls and at the centreline, but these were stable and rarely caused serious problems.

From the p_{O_2} and p_{S_2} calculations carried out, the maximum equilibrium partial pressure of SO_2 in the gases rising from the hearth can be estimated at about $4 \cdot 10^{-4}$ atm. This is an order of magnitude lower than the average concentration of the exit gases leaving the top of the furnace (0.47 per cent), estimated by Barnett (1976) from measured flue gas concentrations corrected for measured quantities of dilution air. It is therefore concluded that SO_2 evolution from hearth reactions is negligible in considering the overall deportment of sulfur in the furnace.

The important conclusion from these arguments is that the maximum sulfur contents of the blast furnace slag and bullion are determined by equilibrium thermochemistry as a particular outcome of the chosen slag composition (with zinc content being the major determinant), the effective operating temperature and oxidation potential in the equilibrium zone. Any excess sulfur reporting in this zone must result in the formation of deleterious ZnS-rich accretions. For a given smelter lead production rate, this constraint determines the maximum amount of sulfur that can be eliminated from the furnace dissolved in bullion. The total amount of sulfur eliminated in hearth products can be varied to some extent by changing the slag/bullion ratio, since the quantity of sulfur contained in the slag is several times that in the bullion. In the Barnett (1976) report, this is by a factor of three; however, varying the slag/bullion ratio for a fixed lead production requires additional energy input in the form of coke. The scope for burning additional coke in a given lead blast furnace is limited by the blast air capacity, which in turn is constrained by the furnace configuration and ancillary equipment capacities. In effect, there are both theoretical and practical constraints on the maximum amount of sulfur that can be eliminated from the furnace via the hearth products.

The proportion of the input sulfur in various charge components reported in the slag and bullion products between 1958 and 1987 was calculated at various times to be in the range of 60–70 per cent, with the balance assumed to leave the furnace as SO_2 or in entrained fume in the exit gases. A re-examination of the data during the period of high sulfur input (via battery scrap, a practice subsequently discontinued) described in Barnett (1976) might suggest some accumulation of sulfur within the furnace in the form of accretions. Because the sulfur content of the exit gases must be formed as a result of reactions occurring within the charge somewhere above the equilibrium zone, as argued, the question now arises as to what these reactions might be, and whether they can be controlled to limit the amount of sulfur passing to the equilibrium zone products.

This question, and particularly that of controlling the sulfur content of bullion, acquired considerable economic importance with the introduction of the furnace process for continuous copper drossing (CDF) in the early 1960s (Peck and McNicol, 1966). The copper-lead-sulfur matte produced by this process was at that time marketed to European custom smelters at a tariff that was heavily biased towards maximising the copper content and minimising the lead content. Accordingly, the chemistry of the CDF required a careful balancing of the Cu/S ratio in the input bullion coming directly from the blast furnace. If the sulfur content were too high, the result was a matte with an excessive content of lead that attracted tariff penalties. If the sulfur content were too low, the moderately high content of arsenic in the bullion caused the precipitation of a high-melting arsenic-rich speiss phase.

The resulting refractory accretions deep in the CDF at the bullion/matte interface caused serious operating problems. As far as the operation of the blast furnace was concerned, prevention of speiss precipitation at the CDF required control of the sulfur deportment between blast furnace slag, bullion and exit gases to provide a Cu/S mass ratio in the bullion within a range of 3/1 to 4/1 as then measured by sampling and analysis. An assumption long held at Port Pirie was that the required level of sulfur in bullion could be achieved by controlling the residual sulfur content of the input sinter by appropriate manipulation of the sintering plant operating variables. This assumption is now examined.

Sinter plant practice and the control of the sulfur content of sinter

Port Pirie sintering practice was always influenced by economic factors, which, until 1968, led to an emphasis on increasing individual blast furnace lead production by optimising sintering practice and by improving furnace configuration. After the commissioning of the slag fuming facility in 1968, there was a further economic incentive to maximise both slag and bullion production together. The long-term aim, always, was to achieve all lead production within a single blast furnace, a goal eventually reached in the late 1970s following the introduction of oxygen enrichment of blast air to the lead furnace (Fern and Jones, 1980).

Prior to 1968, the maximising of bullion production was achieved by maximising the lead content of the sinter to minimise coke consumption, thus offsetting the process-limiting effect of a blast air rate consistent with stable furnace operation. With the introduction of updraught sintering in 1955, there was initially a disastrous deterioration in furnace throughput, identified as resulting from the more oxidised sinter produced by the new process. This was rectified by the addition of coke breeze to the sinter machine feed, which provided a partial reduction of its oxidised lead content. For a sinter containing 52 per cent lead, experimental work showed that an addition of 1.5–2.5 per cent coke breeze reduced the combined oxide lead content to a preferred figure of about 35 per cent (Manson, 1958). Lumsden (1960) subsequently deduced the thermochemical reasons for the successful behaviour of such sinter in the blast furnace. Grant and Cunningham (1971) later confirmed that maximum productivity of the furnace during an observation period from July 1967 to February 1968 required an optimum combined oxide lead content of ~30 per cent (a minimum within the preferred range of 30–35 per cent).

Somewhat surprisingly, the optimum total lead content of the sinter was also found to be a minimum of ~44 per cent (range 44–50 per cent). For many years following the introduction of slag fuming, the level of total lead in sinter was maintained in the range of 42–46 per cent, which provided a generally acceptable compromise between the sometimes conflicting requirements of matte grade and productivity with respect to blast furnace lead bullion and zinc from slag-fuming oxide; however, there were periods of operating excursion – either of sinter plant or blast furnace – that occasionally produced lead bullion of unacceptably high but more usually low sulfur content, as might now be predicted from the factors noted. These invariably led to renewed considerations of sulfur deportment control via the sintering operation without any great appreciation as to how this might be achieved. Attention eventually passed to the upwards adjustment of the bullion sulfur content after leaving the blast furnace (not being constrained by interaction with a high zinc slag), a goal eventually achieved at the CDF itself (Wiltshire, Miller and Bauer, 1989).

With the benefit of hindsight – derived to some extent from the better understanding of Pb–S–O chemistry as applied to melts in the new direct smelting processes arising during the late 1970s – it can be argued that the residual sulfur content of lead sinter is not an independently controllable process variable. The determining factors are the oxygen potential in the molten stage of the sintering process and the kinetics of the combustion process within the sinter bed.

This argument is an outcome of the molten phase thermochemistry that results from the limitation of the oxidised lead content in sinter already discussed. When considering the structure and speciation of the sinter feed to the lead blast furnace, most studies of sinter properties have considered only the highly heterogeneous nature of the solid sinter product created by the relatively slow chilling of the melt during the latter stages of the process on the sinter strand. Using transmitted light microscopy, Manson (1958) found that the Port Pirie updraught sinter product consisted mainly of a glassy silicate matrix containing occasional unaltered inclusions of charge components, lead and lead oxide, ferrites and spinels ($M^{II}M^{III}_2O_4$) of visibly varying types, and minor quantities of melilites ($Ca_2M^{II}[Si_2O_7]$).

Investigations on sinters from the Chimkent plant in Kazakhstan using a wider range of techniques including chemical analysis, microscopy with both transmitted and reflected light, and infrared spectroscopy were carried out in the 1960s, reported in the Russian language and later collated in monographs by Polyvyannyi (Polyvyannyi and Gaivoronsskii, 1969; Polyvyannyi, 1976). The wider range of techniques identified somewhat greater complexity in the set of compounds in their sinter product – a majority of lead silicate glasses, ferrites (zinc, lead and iron), melilites, litharge as free oxide and in pores and cracks in the sinter, and grains of unmelted and partially melted galena. These general groupings were able to be further subdivided into specific mineral types. There is no real incompatibility between these two sets of studies, given the significant differences in sintering practice between the two sites. At Port Pirie, using mainly high-grade concentrates (~70–75 per cent Pb) to produce the optimum oxidised and total lead in sinter (as discussed) while maintaining the desired zinc content of the blast furnace slag, up to 25 per cent of the raw feed to the sinter consisted of recycled granulated slag. This component of the feed would therefore already have been in a glassy but low-lead state. At Chimkent, the concentrates contained a much higher iron content, requiring adequate fluxing with limestone and silica but allowing for no recycled slag component. The similarities in the product sinters suggest a significant homogenisation in the sintering process through component reaction and fusion, followed by the formation and precipitation of complex crystalline compounds by devitrification of the reaction melt during relatively slow cooling on the sintering machine. This process contrasts with the shock chilling of blast furnace slags during granulation, such that to allow study, early microscopy of lead smelting slags required the careful development of the microstructure by slow cooling from the molten state. Sinter bed (gas) temperatures consistently in the range of 1075–1100°C were observed in experiments simulating practice at Port Pirie (Ward, 1959), certainly well above the fusion points of slags with non-metallic lead contents of 35–45 per cent or higher. A discussion in terms of molten state thermochemistry of the question of sulfur deportment control in sinter charged to the lead blast furnace is therefore consistent with observation and practice.

The activities at sintering temperatures of some of the solidified sinter components can be considered in terms of a hypothetical melt with a composition combining that of Port Pirie blast furnace slag with added lead oxide to achieve a concentration of 35 per cent PbO. Oxide activities can be calculated using the regular solution assumption pioneered by Lumsden (1961) and later extended to describe lead and zinc smelting slags (for example, Grant, 1980). The PbS activity can be calculated from the PbO activity and an SO_2 partial pressure estimated from the sinter plant gas analysis adjusted to an oxygen-free basis to approximate the condition applying within the combustion zone of the sinter bed. The results of these admittedly rough calculations are presented in Figure 9. These show that, in principle, the activities of the solid ferrites, magnetite and zinc ferrite, as well as that of lead sulfide, reach a value of one (saturation) in the melt at temperatures well above the liquidus of the major lead silicate glass phase. Thus, the separation of such components identified in solidified sinter product must occur by precipitation from a melt formed at even higher temperatures – such as those reportedly achieved in the sinter bed. This behaviour is consistent with the Chimkent and Port Pirie observations already described.

No significant separate sulfate phase was reported in either the Chimkent or Port Pirie studies, although in the Port Pirie case, routine chemical analyses invariably reported about

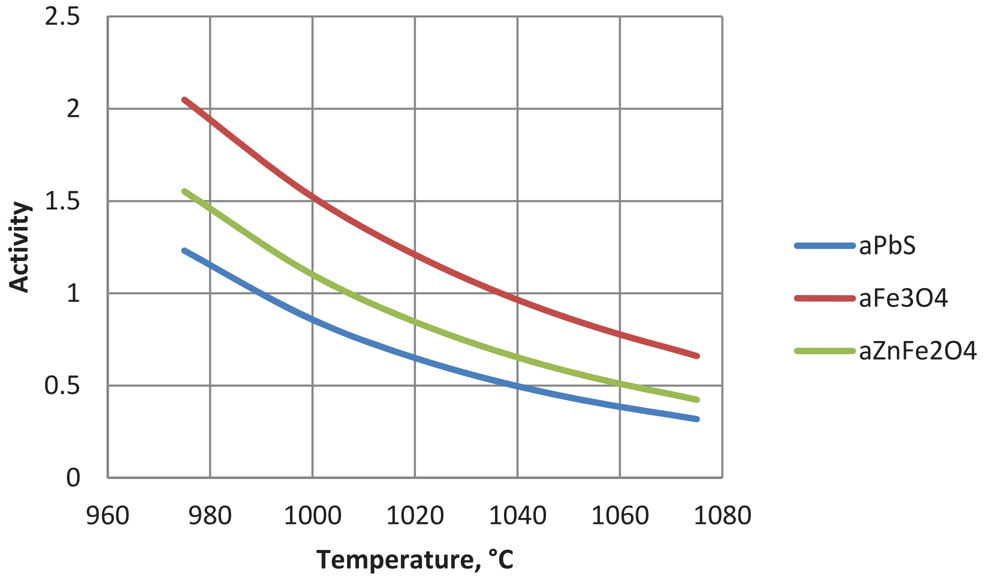

FIG 9 | Melt component activities at 35 per cent PbO in sinter.

a third of the total sulfur present as sulfate. Willis (1980) later discussed experimental evidence showing that there were considerable mutual solubilities of lead sulfate, lead oxide and silicate at sintering temperatures, although their extents were not then known. It might therefore be assumed that the sulfate content of the Port Pirie sinter was present in the glassy phases. Later work by van Huyssteen, Harris and Hancock (1992) using microprobe analysis of Belledune, Canada sinters has identified minor quantities (in total less than five per cent) of various separate phases such as $CaSO_4$, Pb–Ca sulfates and lanarkite (Pb_2SO_5). In this case, the suggested mechanism of formation was by reaction of lime flux with S and Pb fumes rather than precipitation from a molten phase.

Considering now the chemistry of a sintering process phase system containing the reacting species PbO(l)(melt), PbS(s)(melt), $PbSO_4$(s)(melt), Pb(l), O_2(g) and/or SO_2(g), relevant equations pertaining to a potential high-temperature equilibrium can be written:

$$\mathrm{PbS(s)(melt)} + {}^{3}\!/_{2}\,\mathrm{O_2(g)} \rightleftharpoons \mathrm{PbO(l)(melt)} + \mathrm{SO_2(g)} \tag{9.5}$$

$$\mathrm{PbS(s)(melt)} + \mathrm{O_2(g)} \rightleftharpoons \mathrm{Pb(l)} + \mathrm{SO_2(g)} \tag{9.6}$$

$$\mathrm{Pb(l)} + {}^{1}\!/_{2}\,\mathrm{O_2(g)} \rightleftharpoons \mathrm{PbO(l)(melt)} \tag{9.7}$$

$$\mathrm{Pb(l)} + \mathrm{SO_2(g)} + \mathrm{O_2(g)} \rightleftharpoons \mathrm{PbSO_4(s)(melt)} \tag{9.8}$$

for which equilibrium constants applying to the deportment of PbO, PbS and $PbSO_4$ into the melt phase are:

$$K_{9.6} = \frac{a_{\mathrm{Pb(l)}} * p_{\mathrm{SO_2}}}{a_{\mathrm{PbS(s)(melt)}} * p_{\mathrm{O_2}}} \tag{9.9}$$

$$K_{9.7} = \frac{a_{\mathrm{PbO(1)(melt)}}}{a_{\mathrm{Pb(1)}} * p_{\mathrm{O_2}}^{½}} \tag{9.10}$$

$$K_{9.8} = \frac{a_{\mathrm{PbSO_4(s)(melt)}}}{a_{\mathrm{Pb(1)}} * p_{\mathrm{O_2}} * p_{\mathrm{SO_2}}} \tag{9.11}$$

For a sintering procedure operating under steady-state conditions in which the combustion zone moves upwards through the bed at a uniform rate such that these reactions approach a near-equilibrium outcome at constant temperature, the oxygen partial pressure can be calculated from tabulated values of $K_{9.7}$ and a value of aPbO(l) ≈ 0.7, estimated from the composition of Port Pirie slag enriched by PbO to about 35 per cent lead content. The activities of PbS(s) and $PbSO_4$(s) then follow from $K_{9.6}$ and $K_{9.8}$, provided the partial pressure of the reaction product SO_2 is known. The results of standardised pilot-scale tests simulating sinter machine conditions around 1958 were consistent with such a reaction system. Manson (1958) and Ward (1959) reported SO_2 concentrations of 10–12 per cent in product gases and bed temperatures of 1100°C during the steady-state period of the reaction zone passage through the bed in the standard experimental test.

The foregoing discussion indicates that, in respect to S deportment, the chemical outcome of the sintering process is dependent both on the mass balance and the temperatures achieved within the reaction band as it moves upwards through the sinter bed. The intensity of reaction within the band depends on both physical and chemical factors discussed by Manson (1958) and Blaskett (1958). The rate of the upwards movement of the heat front through the bed ahead of the reaction band is controlled by physical heat-transfer parameters of the process (rate of blowing per unit bed area, bed voidage and ratio of the heat capacities of the gas flow and bed solids). These vary only slightly for a given sintering process. Accordingly, the depth of the reaction band depends on how well the rate of chemical reaction is matched to the rate of heat transfer. A rapid reaction rate results in a narrow high-intensity band, a slower rate results in a broader lower-temperature band. The reaction kinetics involve key factors of charge composition and preparation, charge permeability, ignition and airflow during sintering, all of which could be affected by many process operating variables.

The effective heat requirement to produce a given mass of product sinter depends on the heats of reaction, fusion and slag formation, and that required to raise the reactants to the reaction temperature. The fuel to meet this requirement is the sulfur content of the input feed, assuming that the reduction of product lead oxide by the combustion of added coke breeze takes place subsequently at a slower rate than the process of sinter formation and is therefore thermally incidental. It follows that, given the limitation on heat transfer imposed by the physical properties of the bed, there should also be a limitation on the rate of sulfur combustion. This is often expressed as the specific sulfur elimination rate of a sinter machine. At Port Pirie the rate for non-nodulised charges up to 1986 was 2.3–2.5 t/m^2 active grate area per 24 hours, with little variation from year to year. This was achieved from a sinter plant feed of a maximum of six per cent S to produce sinter averaging 1.7 per cent total residual sulfur, ranging from 1.3 to 2.7 per cent. Internal reports (for example, Palumbo, 1986) showed that consistently high residual sulfur contents in poorly fused, friable sinters could be linked with periods of high sinter production rates when attempts were made to exceed the long-established specific sulfur elimination rate.

Experience would also suggest periods of short-term excursion from the desired norm of less than two per cent total residual sulfur. These were usually associated with a temporary loss of control of moisture in the input feed, thus affecting the permeability, heat transfer properties and heat balance characteristics of the sinter bed. It is also probable that disturbances could occur within the return sinter circuit that amounted to 40–55 per cent of the total machine feed during the years 1958–1986. The recycled sinter stream consisted of crushed product sinter – partly roasted fines screened from the product – mixed with the entire output of collected combined fume recovered from the sinter plant and blast furnace gases slurried to produce a wet filter cake (partly dried on mixing with the hot return sinter). It also contained the prescribed amount of coke fines. While the particle sizing of the components of this stream was carefully controlled, its chemical composition and calorific value, obviously, were not. The resultant variation in the intensity of the combustion process inevitably leads to some variation in sinter quality at Port Pirie, however that might have been defined.

While there was always agreement that blast furnace productivity and ease of operation constituted the ultimate arbiter of sinter quality, there was never any consensus as to what might be an appropriate measure of the input sinter quality. Various measures such as size range, brittleness (as measured by a drop shatter test), toughness (as measured by a rumble test), reactivity, specific surface area and residual sulfur content all proved inconclusive, as did many statistical investigations into cause–effect relationships between sinter plant operating variables and one or more of these criteria. In practice, the aim was to produce a well-fused product of suitable size range, porosity and hardness – subjective criteria at best – but with experienced management, a consistent product could be produced with little variation.

In summary:

- managing the sintering process has the prime requirement of meticulously controlling the slag-forming components of the sinter feed within a specified ratio of total lead to slag in the product sinter
- quality control of the product also requires limiting the proportion of lead content in oxidised form and certain subjective physical qualities of the product sinter generally agreed to be necessary for the efficient physical, chemical and economic operation of the subsequent blast furnace process and further ancillary processes
- successfully achieving these physical and chemical outcomes via combustion reactions in the sinter bed requires careful operational control of many variables to achieve consistent continuous reaction conditions of mass balance and temperature
- within the reaction system, deportment of sulfur between exit gases and the molten mixture within the reaction band on the sinter machine can be inferred from the thermochemistry of the Pb–S–O system
- variations in the physical quality of product sinter suggest variations in the intensity of reaction conditions, which must also affect the outcome of reactions in the Pb–S–O system, specifically in respect of oxide, sulfide and sulfate ratios.

Given the emphasis on sinter quality as the main determinant of blast furnace performance at Port Pirie, it can be concluded that sinter sulfur content and/or sulfate/sulfide ratios could not have been independently controllable parameters.

Eliminating sulfur from the blast furnace as SO_2

Within the blast furnace, the sinter charge reacts with reducing gases under conditions of increasing temperature and decreasing oxygen potential as it passes towards its final transformation into the molten bullion and slag products in the hearth of the furnace. Its sulfur content is distributed between that in the exit gases in the form of SO_2 and as a component of entrained fume, and that dissolved in bullion and slag. The distribution of sulfur in the products varies with the mass ratio of slag to bullion, since the concentration of S in the slag is several times that in the bullion. An accurate mass balance for sulfur is quite difficult to determine in practice, because the furnace charge may contain several sulfur-bearing constituents. In carefully observed campaigns at Port Pirie in 1972 and 1973 (Barnett, 1976), sources of sulfur included those as a component in coke, recycled CDF slags, recycled slags from early operations with varying sulfur contents up to four per cent and battery scrap. In the final ten-day campaign using sinter with 44–48 per cent lead content, the resultant deportment was ~45 per cent to slag, ~15 per cent to bullion, ~35 per cent as SO_2 and ~5 per cent in fume. Earlier attempts to assess the sulfur deportment suggesting that the fraction reporting as SO_2 could be as high as 40–45 per cent were probably in error because of a then unrecognised difficulty in determining the sulfur content in the bullion phase. This became apparent only after the commissioning of the continuous CDF process in 1963 when the sulfur content of the CDF (products, matte and slag) was shown to exceed the apparent content of the input blast furnace bullion by some 40 per cent, an error eventually found to be an outcome of rapid phase separation during the bullion sampling operation.

For the purposes of this discussion, only the behaviour of the sulfur content of sinter – the major (~90 per cent) source – will be considered.

The evolution of SO_2 on heating sinter in an atmosphere of nitrogen was mentioned by Haney and Hopkins (1954) when describing laboratory experiments at Port Pirie. With a progressive increase in temperature, their tests showed that elimination of SO_2 from sinter commenced at about 750°C rising to a maximum rate at 850°C, and was still significant at 900°C. Subsequent experiments (Ward, 1960) were aimed at identifying the mechanism of the evolution of SO_2 at 750°C in a stream of oxygen-free nitrogen. Changes in sample mass were correlated with SO_2 evolution and changes in the ratio of sulfide to sulfate sulfur.

Two distinct periods of reaction were observed – an initial rapid weight loss and SO_2 evolution identified as:

$$PbS + 2PbO = 3Pb + SO_2 \tag{9.12}$$

during which the sulfate content of the reaction mass did not alter, followed by a lengthy period of slower reaction where the sulfate content diminished to less than half its original value. The second phase of reaction was then ascribed to lead sulfate reactions, for example:

$$\tfrac{1}{2}PbS + \tfrac{1}{2}PbSO_4 = Pb + SO_2 \tag{9.13}$$

The overall ratio of total sulfur to sulfate sulfur decreased from 2.55 to 1.9. The observed volatilisation of PbS was shown to be a significant contributor to the overall weight loss of the sinter samples under the experimental conditions.

Gas analyses made during the 1970s observation campaigns at Port Pirie showed that the gases leaving the charge averaged 0.5 to 0.8 per cent SO_2. This corresponds approximately with the equilibrium partial pressures for the reactions in Equations 9.12 and 9.13 in the range 700–800°C with pure solid reagents; that is, about the temperature at which reactions evolving SO_2 had been shown to occur to a significant extent. The equilibrium concentration, however, is much greater than that measured in the laboratory experiments mentioned. It is therefore reasonable to conclude that, at 750°C, the kinetics of reaction limit progress towards an equilibrium outcome. Thus, most of the SO_2 concentration in the exit gases must be generated at higher temperatures lower in the furnace where much higher reaction rates would be expected, and the equilibrium partial pressures would be two or three orders of magnitude greater.

These early laboratory experiments merely showed that in a non-reducing atmosphere at a lower oxygen potential than that of the sintering process, PbS could act as a reductant for PbO and $PbSO_4$ at temperatures as low as 700–800°C. Within the blast furnace, however, this temperature range is also when reduction of the oxidised sinter components by CO begins to occur at a significant rate (Haney and Hopkins, 1954; Polyvyannyi *et al*, 1971), so that there is competition for the available PbO and $PbSO_4$ between reductant CO and PbS in the gas phase and PbS in the incipiently molten phases in the charge.

Low-temperature reduction experiments were carried out on a standardised Port Pirie sinter using pure hydrogen as the reductant at 600°C, 700°C and 800°C (Ward, 1959). The aim was to develop a test for the low-temperature reducibility of lead sinter, a property earlier postulated by Haney and Hopkins (1954) as critical for optimum blast furnace performance. In these experiments, the rates of change of the sulfate and sulfide concentrations were followed, together with the rate of reduction of the combined oxidised lead compounds. The results at the three temperatures are compared in Figure 10. While these experiments under such highly reducing conditions were not intended to simulate the behaviour of lead sinter reduction in the blast furnace, they are of interest in that they span the temperature range at which the major glassy silicate-phase component of sinter would be expected to become molten. The results point to differences in the decomposition mechanisms of the sulfide and sulfate components in the solid and liquid states.

The important observations are:

- at 600°C, the sulfate appeared to have been stoichiometrically reduced to the sulfide, resulting in an increase in sulfide concentration
- at 700°C, the increase in sulfide concentration was less than the decrease in sulfate concentration
- at 800°C, both sulfate and sulfide concentrations decreased.

On the evidence of Polyvyannyi (1976), as a result of diffusion factors the reduction of lead silicate glasses by CO differs from that by hydrogen only in terms of the initial reaction rate constant. Accordingly, the following discussion assumes that the behaviour of sulfur compounds in sinter during reduction by CO would be similar to that in the hydrogen reduction experiments.

At 600°C, with all reagents in the sinter in the solid state, it would appear that the major mechanism of decomposition of the sulfate is direct reduction to the sulfide:

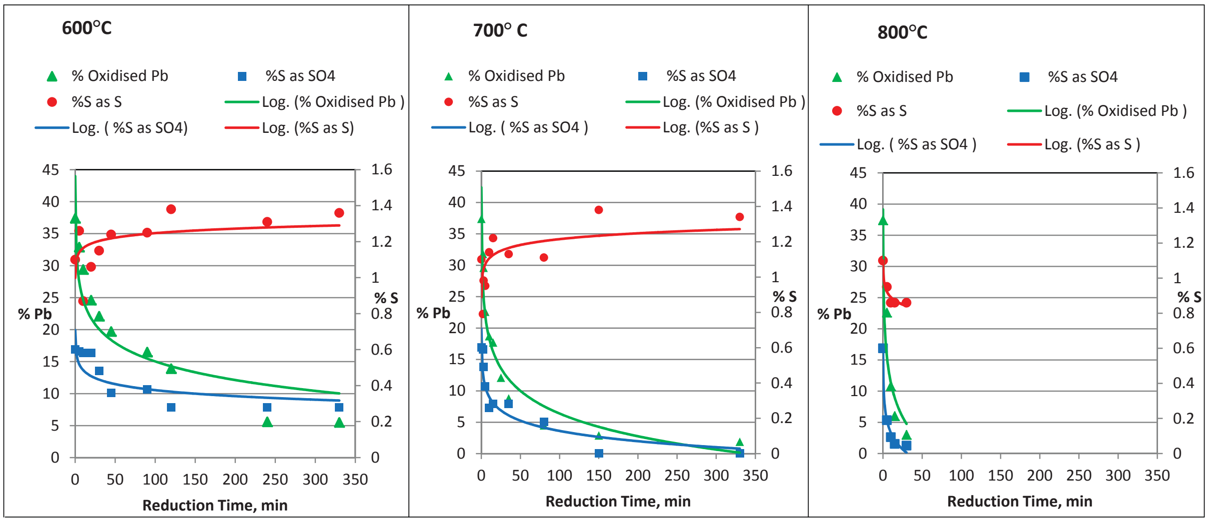

FIG 10 | Reduction tests on a 'standard' Broken Hill Associated Smelter (BHAS) laboratory lead sinter (Ward, 1959) using pure hydrogen reductant. (Trend lines generated on an assumption of first-order reaction rates for the individual components.)

$$PbSO_4 + 4CO = PbS + 4CO_2 \tag{9.14}$$

Since the glassy phase in sinter should already be saturated with sulfide, the product of reaction should be PbS, additional to the separate solid phase noted by Manson (1958). In that there was no net change in the total sulfur content of the sinter, it would seem that no evolution of SO_2 took place at this temperature under the strongly reducing conditions.

Both the investigations in nitrogen atmospheres and under strongly reducing conditions suggest that a homogeneous reaction at temperatures as low as 700°C can take place according to the reaction in Equation 9.13 between sulfide and sulfate species with the evolution of SO_2. The behaviour of sulfur compounds in sinter at 700°C and above could therefore be ascribed to a combination of an initial dominance of the heterogeneous reduction in Equation 9.14 followed by the slower homogeneous reactions in Equations 9.12 or 9.13, or both. The summary reaction could then be expressed as:

$$PbSO_4 + n\,PbS + 2(n+1)\,PbO + 4CO = 3(n+1)\,Pb + (n+1)\,SO_2 + 4CO_2 \tag{9.15}$$

In such a reaction equation, the value of *n* may vary according to the reaction kinetics of the component reactions; for example, from positive in the case of the 800°C experiment, to negative at 700°C and to a minimum of -1 at 600°C. If, however, the rate of reaction of PbS with PbO according to the reaction in Equation 9.12 is sufficiently fast so that there is no net accumulation of PbS in the product and PbO reacts preferentially with CO as in the 800°C reduction experiment, the outcome of the decomposition of lead sulfate is, effectively:

$$PbSO_4 + 2CO = Pb + SO_2 + 2CO_2 \tag{9.16}$$

which is the form assumed by both Lumsden (1960) and Barnett (1976) in calculating the contribution of sulfate decomposition to the total heat balance of the furnace. In that context, however, the mechanism of sulfate decomposition was irrelevant and only the form of the end products Pb and SO_2 was thermally important.

Table 7 is a sulfur balance for the Port Pirie furnace based on that reported by Barnett (1976). Corrected values allowing for known inaccuracies in bullion and fume analyses have been used. About 96 per cent of the deportment of input sulfur to output products is accounted for, which is reasonable for the combination of measured and estimated industrial data acquired at the time of the 1972–1973 observation campaign.

The emission of sulfur as SO_2 is somewhat less than the total input of sulfate sulfur, but approximately equals that entering as the sulfate content in sinter. This would appear to be consistent with Equation 9.16. An alternative interpretation, however, could be that

TABLE 7

Sulfur balance at the Port Pirie blast furnace 1972–1973.

	Expressed as % of total input				
Input	Total S	S as sulfide	S as sulfate	Output	
S in sinter	70.5	41.0	29.5	S in slag	43.7
S in quarried slag	21.7	21.7		S in bullion	14.1
S in battery scrap	4.9		4.9	S in fume	7.6
S in copper drossing furnace slag	0.7	0.7		S as SO_2 in gases	30.4
S in coke	2.0	2.0		Unexplained	4.2
Total	100.0	65.5	34.4	Total	100.0

the sulfur content of battery scrap as free sulfate was rapidly reduced to the sulfide by the reaction in Equation 9.14 and, not being in intimate contact with any oxide, remained in that form. The sulfate present in the sinter fraction of the charge would have been reduced at a slower rate due to its lower activity as a component in the glassy silicate phase and the dependence of heterogeneous reduction by CO on the diffusion of reactants within the glassy phase to the reaction interface. This suggests that for the particular set of circumstances prevailing at the time, the formation of SO_2 could have been by the reaction in Equation 9.16 – as indeed was assumed by Barnett (1976). In terms of the mechanism underlying the reaction sequence summarised in Equation 9.15, such an outcome would have required that the rate of reduction of sulfate to sulfide by Equation 9.14 was exactly matched by the rate of consumption of PbS by the reaction in Equation 9.12. There could be no decrease or increase in the concentration of PbS in the reacting mixture; otherwise there would have been no match between the rate of decomposition of the sulfate and the production of SO_2.

In respect of Equation 9.15, factors affecting reaction kinetics in the blast furnace throughout the charge temperature gradient in the range, say, from 600–1000°C are the rate of temperature change, the changing CO_2/CO ratio and the relative amounts of the three lead species in the mass balance.

The charge temperature gradient is governed by:

- physical rates of heat transfer from the hotter gas phase to the charge surface, and from the charge surface to within the charge matrix
- the balance of heats of reaction between the generally endothermic desulfurising reactions
- the rate of mass transfer of zinc vapour to the charge surface and exothermic reversion to zinc oxide thereon
- the exothermic reduction of metal species by CO.

The CO_2/CO ratio is governed by:

- the CO_2/CO ratio in gases rising from lower in the furnace
- reduction reactions involving CO and reducible metal species – lead to lead metal and ferric iron to ferrous
- the reversion of zinc vapour to zinc oxide by reaction with CO_2
- the kinetics of reduction of sulfates according to Equation 9.16.

The mass balance with respect to sulfur species is governed by:

- the kinetics of reduction of PbO by CO and its availability for reaction with PbS
- the kinetics of reduction of $PbSO_4$ to PbS
- the kinetics of reaction between PbO and PbS, occurring both as separate species and as components of the glassy phase within the sinter
- the kinetics of reduction of sulfates according to Equation 9.16.

Whether or not such a complex (but, nevertheless, component) thermochemical system can be realistically modelled surely depends on the feasibility of developing an acceptable overall model for the major interacting phenomena of the reduction chemistry within the lead blast furnace.

Implications for Process Modelling

10

Chemical process modelling aims to provide a means of describing, from known first principles and simulation criteria, the actual performance of a reactor as measured and observed during practical operation. Such modelling may provide a reconciliation of theory with observed practical outcomes, better general understanding of the complex interaction of input variables, identification of critical control factors and extrapolation towards improved or alternative means of operation.

For the lead blast furnace, previous discussion has shown that links between criteria measured in the laboratory for simplified component systems under controlled conditions and the behaviour of the much more complex real systems have been difficult, if not impossible, to establish. All models to date have relied on analogy with other processes, application of developments in the state of the art of metallurgical thermochemistry, the use of data from statistically designed industrial-scale experiments and outcomes of changes to operating practice and/or furnace design. All, however, rely on assumptions and linking theories that are open to criticism and revision.

At Port Pirie, Lumsden's 1960 model of the lead blast furnace led to a greater understanding of the thermochemical principles governing its operation, in particular the necessity of balancing the heating and reduction functions of the coke fuel with the inherently endothermic heat requirements of slag formation and melting and counteracting exothermic reduction reactions. Despite its several unproven assumptions, the model provided a focus for the statistical examination of sinter plant and blast furnace control variables influencing their combined technical and economic performance. It also identified certain key operational parameters which, at the time, were either not monitored or beyond the scope of then current instrumentation technology – specifically the exit gas CO_2/CO ratio, jacket heat losses, slag and bullion temperatures and oxygen potential and their relationship to short- to medium-term production rates. By the early 1970s, such instrumentation had become available – at least in principle (BHAS was unable to successfully adapt commercially available oxygen potential probes to lead smelting conditions). Two separate observation campaigns of about two weeks duration were carried out in January/February of 1972 and 1973 using a mixture of additional installed and temporary instrumentation to gather sets of data on a one- to two-hourly basis. Furnace top conditions, sinter lead analyses and recycle feed quantities (reclaimed dump slag, refinery drosses, battery scrap) varied significantly both within and between campaigns. The results were collated in an internal BHAS report by Barnett (1976). Heat and mass balances for average conditions within each campaign showed consistent agreement within one per cent between measured heat inputs and measured and calculated heat outputs.

A general heat and mass balance model was then developed, taking into account interrelationships between process variables statistically determined from the data sets. The model was designed primarily for the prediction of production parameters determining the cost of melting within the blast furnace the additional reclaimed slag (of variable composition dating back to the 1890s) required to optimise zinc production via the newly commissioned slag fuming plant. The model was experimentally successful, enabling the prediction of coke requirements for a given charge mixture and a given set of operating conditions. It was later used to evaluate the results of a full-scale trial of oxygen enrichment in the blast, leading to the investment in a small on-site oxygen plant dedicated to this purpose. A description of the BHAS adoption of oxygen enrichment practice is described in Fern and Jones (1980).

The model was not incorporated into the overall works' economic model because of the several measurements of output parameters requiring involvement of limited manpower resources for manual determinations; for example, jacket flows and temperatures, off-gas temperatures, flows and compositions and oxidised lead content of the input sinter.

A somewhat surprising outcome of the experimental campaign was the revelation of short-term fluctuations in hourly observations compared with those in routinely logged records based on averaged eight-hourly shift observations and analysis of cumulative samples. Importantly, these fluctuations related to production rates of slag and bullion, product temperatures and bullion compositions.

In respect of production rate analyses, the regression analysis (both linear and non-linear) of the short-term data considered the slag and bullion only as separate (rather than paired) identities, with an emphasis towards factors that may have influenced the sulfur deportment. With the benefit of hindsight, an examination of paired slag and bullion analyses together with temperatures could have yielded information as to the short-term variation in the hearth zone oxygen potential via the activity of the ZnO content of the slag and the activity of the Zn metal content in the bullion. At the time, however, the available methods for the calculation of both these quantities were of uncertain validity. Nevertheless, an examination of the partition mass ratios of the various elements reporting in both slag and bullion could have been interesting.

As it is, the regression analysis provided an oversimplified set of equations giving a reasonable approximation to relationships between input and output variables observed within the 10-to-12-day periods of examination. A notable difference between the results of these observation campaigns and previous statistical analyses (for example, Grant and Cunningham, 1971) lies in the fact that significant regression relationships showed that the blast rate explained only 35 per cent of the variation in bullion and slag production rates, compared with over 60 per cent in the earlier long-term studies (three to six months) using averaged eight-hour data. Barnett (1976) claimed that this could have been due to the blast rate varying only slightly during the 10-to-12-day periods of study. It is now suggested that the unexpectedly large unexplained variation was real, reflecting the observed short-term (hourly) production variations mentioned. These could have been due to variations in the rate that coke in the charge arrived in the tuyere zone, resulting also in changes in oxidation potential leading to the observed variations in the concentration of the reducible species Fe and Zn in the bullion.

This discussion is perhaps trying to be wise after the event, but emphasises that it is simply not valid to extrapolate the regression equations derived from a given limited study outside the range of known inputs.

That the model failed to fully and satisfactorily account for the variation in productivity indices (tonnes bullion and slag per day, kg C/t charge, m^3 air/kg C – see Table 7) between the two sets of observation campaign data is hardly surprising. Simple linear and second-order relationships between operating variables and production outcomes can hardly be representative of the complex thermochemical relationships suggested by Lumsden. Although the statistical model failed in this respect, it did confirm that the heat balance of a furnace is always maintained, regardless of how well or badly the furnace is operating. Potential imbalance is offset by variation in the exit gas temperature and CO_2/CO ratio.

The fact remains, however, that the predominant factor limiting the productivity of a lead blast furnace is the coke combustion rate as determined for a particular charge composition by the blast air oxygen content and throughput rate (~60 per cent explained variation – see earlier discussion of Port Pirie statistical investigations by Grant and Cunningham, 1971). Both the coke rate and the blast rate are directly related to the physical and thermochemical characteristics of the input sinter in order to arrive at a consistent final product outcome. It may be possible to define lead blast furnace operation in terms of reduction mechanisms involving reaction thermodynamics, kinetics and heat and mass transfer dynamics. Nevertheless, the economics of blast furnace operation are directly and importantly related both to individual furnace productivity and coke consumption.

Blast rate and productivity prediction

The achievable blast rate in a lead blast furnace is constrained by geometrical factors in order to achieve adequate penetration and coke combustion at tuyere level without causing high-temperature reactions to rise to the surface of the charge – the hot-top condition historically associated with lead blast furnace practice. Green (1977) describes the experiments at Port Pirie in the 1930s that established tuyere spacing, furnace width between opposing tuyeres and charge height, leading to the double tuyere row configuration unique to the Port Pirie operation. The extra width allowed by the double tuyere row resulted in a welcome but perhaps unintended consequence of better operator control of accretion and potential bridge formation.

The blast rate is also physically limited by the softening and fusion behaviour of the sinter component of the charge, together with its distribution with respect to the coke component at charge temperatures upwards of 1000°C. Softening is directly related to the tendency towards bridge formation within the charge, leading to variable permeability and hence variable gas flows at a given blast pressure. Blowing – the surface break-through and escape to the environment of a localised high-velocity stream of hot fume-laden gas from the furnace – is a frequent and serious outcome of charge softening and bridging. It is ameliorated but never entirely eliminated by careful operator attention. The remedy ultimately employed at Port Pirie to stop a 'blow' is shaking – a complete cessation of the blast that causes the collapse of voids in the charge generated by bridging. This action causes a drop in charge permeability and hence throughput, demonstrated statistically by a correlation between slag production rate and the frequency of the shaking procedure (Barnett, 1976). References cited earlier in the discussion show that, experimentally, a softening temperature can be measured by laboratory testing and is related to sinter chemistry via its crystal structure. While such tests can point to preferred sinter/slag compositions, any formal relationship between softening temperature and charge permeability remains undefinable. Charge permeability for a given sinter composition can also change with time. Variable start-up conditions after a rebuild last only a few days and are characterised by high blast rates at low pressures, high throughput but also high residual lead in slag. This is followed by a long period of 18–36 months of acceptable productivity and lead recovery under controlled conditions that gradually deteriorate to the point of shutdown for removal of deep accretions, hearth repair and general routine maintenance. For the Port Pirie operation, then, long experience has shown a complex interaction between blowing rate, coking rate, sinter composition and softening behaviour, and both routine and reactionary operator intervention to optimise productivity, together with maintaining occupational hygiene and environmental control requirements at the charging floor level in the open-top lead blast furnace design.

Other operations are known to function with continuous hot-top conditions, usually enclosed within a sealed offtake hood. Oldright and Miller (1936) referred to offtake gas temperatures of over 500°C for a relatively low burden height operation at Kellogg compared with other North American plants. A description of the operation of the enclosed full-scale furnace at Chimkent with and without blast preheat and oxygen enrichment (Elyakov, Ovcharenko and Polyvyannyi, 1971) reveals specific productivity rates (t/m^2.day) more than double those achieved at Port Pirie but with average offtake temperatures of 500°C and above. The diagram in Polyvyannyi (1976) of this single tuyere row furnace reveals substantial structural differences in respect of charging and gas offtake equipment compared with the open-top Port Pirie furnaces. Hot-top lead blast furnaces were personally observed by the author in Europe during the 1970s.

There are, therefore, significant differences in blast furnace smelting intensity – both between and within operating sites – that reflect differences in charge column height, furnace geometry and operating practice. These directly interact with the process thermochemistry and reduction kinetics.

The Lumsden (1960) model avoids this difficulty to some extent by commencing calculations on the basis of a thermodynamic equilibrium achieved per mole of carbon burned at the tuyeres. It uses average sinter and slag compositions from a stable production period to determine heat and mass balances in accordance with measured conditions. The length of such a stable production period is open to conjecture. Within the relatively short (about two weeks) observation campaigns described by Barnett (1976), differences in productivity indices observed were, statistically, only marginally significant. Yet in the year between the two campaigns, there were major differences on the same furnace as shown in Table 8 (in both cases maximum productivity was sought).

Effectively, the Lumsden model can predict comparative furnace performance of sinter with varying slag/oxidised lead ratios for a given combustion rate at the tuyere zone. While seeking possible explanations for variations in performance (for example, through

TABLE 8

Variation in Port Pirie No 2[a] blast furnace indices (Barnett, 1976).

	Campaign 1 (February 1972)	Campaign 2 (January/February 1973)
Exit gas CO_2/CO ratio	1.5	2.0
Cooling water (% contribution to the overall heat balance)	9.4	14.2
Pb production (t/d)	378	493
Slag production (t/d)	420	635
Equivalent % Pb in sinter	45.8	44.1
Recycled dump slag (lump)/charge (kg)	0	272
Calc top gas temp (°C)	245	149
Slag, lead temp (°C)	1175	1164
Surface conditions	Poor, hot sticky tops	Reasonable

a. As referred to by Barnett (1976), this is the modified furnace described by Fern and Jones (1975). Blast furnaces 3 and 4 retained the 1947 configuration at that time (Green, 1977), while No 1 had been decommissioned.

thermal outcomes leading to charge fusion and compaction), the Lumsden model cannot quantify their effect or consequent influence on subjective operator decisions.

It is concluded that interaction between physical and chemical behaviour in the charge remains undefinable and incapable of rigorous mathematical modelling. Experience derived from observation, engineering development and statistical studies remains paramount in determining furnace productivity.

Defining reaction outcomes in the furnace shaft

The lead blast furnace is a counter-current flow reactor. Cold, solid feed materials and carbon fuel/reductant enter and product gases of variable enthalpy leave at the top. At the bottom, cold air (often enriched with oxygen) is injected into the reaction mass to produce an upwardly moving reduction gas stream. Product slag and metal leave at high temperatures. Heat and mass transfer together with thermochemical reaction between the rising gas stream and descending charge materials take place along the resultant differing temperature gradients of the charge and gases. Reaction rates between gases and charge materials are controlled by temperature-dependent mechanisms. Observation, experience and industrial- and laboratory-scale experimental evidence led to the concept of a zonal reduction profile as described in Section 8, with each of three reaction zones differing according to temperature range and reaction mechanism.

In the upper reduction zone, reduction of the solid-state lead species lead ferrite and free lead oxide takes place substantially to completion. In the lower reduction zone, the reduction of liquid-state lead species, mainly silicates, takes place to an end point dictated by the underlying equilibrium between gas, slag and bullion phases. Slag-forming species here initially remain in the solid state, forming a lattice that supports the reducing liquid silicates, but which eventually melt at higher temperatures to form a slag. In the equilibrium zone, the air blast and coke react to form a reducing gas mixture in thermal and chemical equilibrium with the product lead and slag phases. The progress of reaction in each zone is dependent on the compositions and temperatures of reactants entering from above or below, or both.

At the stockline (the entrance to the upper reduction zone A), the boundary conditions of outlet gas compositions and inlet sinter and coke compositions are reasonably well known. The reversion of zinc vapour is complete at this point. The exact phase composition of the input sinter in terms of its detailed solid phase analysis (for example, following van Huyssteen, Harris and Hancock, 1992) is not possible as a routine measurement. However, an approximation to evaluate relative amounts of reducible lead compounds by the methods described in Zhao *et al* (2008, 2010) using the program FactSage® is feasible. The range of outlet gas compositions and temperatures has been determined by Barnett (1976) for Port Pirie conditions.

At the outlet at the base of the furnace, the equilibrium temperature and liquid-phase compositions are known, while the heat balance for the equilibrium zone allows a calculation of the gas phase, metal and slag compositions, and temperatures at the boundary between the equilibrium zone C and lower reduction zone B (as in Lumsden, 1960).

Defining the boundary conditions at the crossover between the upper and lower reduction zones A and B presents difficulties for lack of any experimental determination, at a nominated boundary charge temperature, of either the corresponding gas phase temperature or composition. A boundary with a temperature of 1000°C might be arbitrarily selected, as by Lumsden, as being the temperature at which the gasification of coke by reaction with the CO_2 content of the gases ceases. However, this was chosen purely for the purpose of calculation, allowing an assumption of equilibrium within the sinter phase in the lower reduction zone to continue and, further, to assume that reduction of all lead compounds had been completed in the upper reduction zone. In reality, as demonstrated by the Chimkent and Belledune experiments, the majority of the oxidic lead reduction (that of liquid-phase silicates) has yet to occur by the time this temperature has been achieved. Accordingly, it is suggested that an appropriate boundary condition might be that at which the reduction of liquid lead silicate commences (around 850–900°C). While this allows the temperature and composition of the mainly solids charge to be set, the temperature and composition of the gas phase remain unknown, in particular the relative proportions of CO, CO_2 and Zn vapour that are dependent on the outcome of reactions within the lower reduction zone.

A first estimate of the gas temperature and composition at this boundary is possible via heat and mass balances over the upper reduction zone A. The rise in charge temperature and the heat of reduction of lead oxide and lead ferrite are known. The moisture content of charge components is also known, as in Barnett (1976) where the heat required to evaporate charge component moisture amounted to six per cent of the total energy balance of the furnace. These quantities are balanced by heat transfer between gas and charge and by the completion of zinc reversion in the gas phase with attendant changes in the CO_2/CO ratio. A major unknown in this equation is that of physical heat transfer. Methods of calculating heat transfer between gas and charge in a lead blast furnace were employed by Zhao (1993) and Hussain and Morris (1989). These references suggest that the contribution of physical heat transfer to the balance can be calculated, in turn allowing an estimation of the extent of balancing thermochemical zinc reversion. Some uncertainty in such a balance arises from factors of furnace geometry involved in estimating the physical heat transfer. For this reason, the outcome of the upper reduction zone heat and mass balance provides only a first estimate of the boundary conditions. This estimate, however, now allows a further heat and mass balance over the lower reduction zone B. Iteration between the overall heat balances of both reduction zones should then enable the refinement of the temperature and concentration conditions of all phases at the interface.

If it is concluded that boundary conditions between the three defined reaction zones can be calculated with reasonable certainty, process modelling now requires considering the sequence of events within the two reduction zones A and B. This is most important in zone B, in which there is a progressive transition of partly reduced input charge to fully defined products in the equilibrium state.

Discussion in prior sections concludes from observation and experiments that the majority of lead reduction in the furnace takes place from molten silicate phases in the temperature range of the lower reduction zone B. Here, the reduction of lead species by Zn vapour as well as CO must be taken into account since, assuming an equilibrium lower boundary condition at 1150°C, the estimated partial pressure of zinc vapour in the gases is numerically high and very close to that of CO. Holliday, Shoebridge and Firkin (1980) observed that in the ISF, zinc oxide formed by the reversion reaction appeared on and within the sinter in the form of acicular zincite crystals, a particular form associated with the oxidation of gaseous phase zinc also typical in the slag-fuming process. For the lead furnace, however, the results of Polyvyannyi *et al* (1971) tabulated in Table 1 suggest some reaction with charge components to increase the zinc content in the silicates, also as zinc ferrite and only to a minor extent as a separate zinc oxide phase. Insofar as the spinel, zinc ferrite, forms part of the skeletal structure contributing to the high-temperature strength of lead blast furnace sinter, this outcome of the early reduction behaviour of oxidised lead components may explain the raised softening temperature of partially reduced sinter noted by Haney and Hopkins (1954). In any case, the heat of reduction of liquefied sinter components is released in the sinter in the temperature range 1000–1150°C, rather than as proposed by Lumsden (1960) as limited to temperatures below 1000°C. The kinetics of reduction by zinc vapour are unknown, however, as is the partial pressure of zinc at the reaction surface of the charge, which Lumsden identified as a factor determining the rate of zinc migration to the reaction surface.

Furthermore, the sequence of crystallisation of the variably constituted phases in lead sinter described by van Huyssteen, Harris and Hancock (1992) suggests that as the temperature of the sinter component of the charge rises, the amount and composition of reducible liquid-phase lead silicates in contact with the reducing gas phase must change, eventually reaching the point where a true molten slag phase develops near the lower boundary.

The reduction of metal oxides by CO must inevitably have some effect on the CO_2/CO ratio of the gas phase, and hence on the kinetics of the zinc reversion and carbon gasification reactions. As a result, it is not valid to consider such a reduction as a simple superimposition on the hypothetical base case calculated for Lumsden's lead-free furnace reaction zone in which the gasification reaction:

$$CO_2 + C \rightarrow 2CO$$

was the overall rate-controlling step. Fundamental to Lumsden's argument was that all other compounds remained at equilibrium with the changing gas phase down to a temperature of 1000°C, and rates of heat and mass transfer between gas and charge were sufficiently fast that both phases remained at the same temperature. Experiments now show Lumsden's concept to be invalid. Not only does the majority of lead reduction persist into this lower reduction zone, but a state of both thermal and chemical equilibrium between gas phase and charge components cannot exist under the 850°C boundary conditions involving the presence of most of the original input lead as liquid silicate.

In the 850–1150°C temperature range of the lower reduction zone B, a much more complex situation arises as soon as lead reduction and other reactions occur between the liquid components of the charge and rising gases.

There may be two or even three possible initial reaction scenarios depending on (largely unknown) rate-controlling mechanisms prevailing at given temperatures within the charge column. The first arises if the rate of melting lead compounds is controlling so that oxidic lead is reduced as quickly as it appears in the liquid state. The second is if the chemical rates of reduction are always rate-controlling under circumstances where the rate of new oxidic lead reporting in the liquid phase is greater than its rate of reduction. A possible third scenario is if there is a transition from melting rate control to chemical rate control as the temperature rises.

Melting rate control

The possibility of melting rate control within the lead blast furnace does not appear to be mentioned in any of the papers so far discussed. Nevertheless, it could provide an explanation for the apparently poor rate of reduction of the lead silicates relative to charge depth in the Chimkent pilot-scale experiment illustrated in Figure 6. As pointed out in previous discussion, the residence time available for charge heating and reduction in that experiment was significantly shorter than in industrial-scale operations. The absence of any charge temperature measurement does not allow a conclusion to be made as to whether the silicate phase would have been fully molten or not, even though gas temperatures were high. The technique of sampling and analysing the charge after freezing could not have differentiated between solid and liquid silicate phases that may have been present at temperatures prevailing during the experimental period.

If in normal blast furnace operation the melting rate is fully controlling and oxidic lead is reduced as soon as it is formed in the liquid state, the reduction kinetics applying to reaction of a fully molten slaggy phase with a gas phase are no longer relevant. Modelling therefore depends only on being able to predict (for a given temperature increment in the charge) the rate of formation of the liquid phase caused by heat input derived from physical heat transfer and the various heats of reaction. This is easier said than done, however, since van Huyssteen, Harris and Hancock (1992) have shown that the composition and presumably the melting points of the low-melting silicates in a sinter are highly variable and therefore not predictable.

An in-principle model might be developed via application of the FactSage® technique used by Zhao *et al* (2008, 2010) to determine the changing-phase makeup of a given sinter. This would be achieved in terms of the equilibrium properties of known pure chemical species as temperature and the degree of reduction increase.

Chemical reaction rate control

If chemical rates of reaction control the overall rate of reduction, the kinetics of several possible reduction reactions occurring simultaneously must be taken into account, together with zinc reversion and, above 1000°C, carbon gasification. The question as to whether the reduction of different reducible species takes place as a summation of individual rate-controlled reactions occurring simultaneously but independently, or whether there is an influence of equilibrium interaction between species in the molten state on the reaction's outcome in this temperature range is of some importance.

All of the more recent investigations consistently reach the conclusion that the liquid-phase reduction of lead-bearing oxide melts by a gas of low oxygen potential is chemically rather than diffusion controlled (as assumed by Lumsden). A likely reduction scenario must involve the difficulties of defining kinetic parameters under dynamically changing conditions of interfacial areas, gas and liquid-phase temperatures, compositions and activities. Furthermore, the reduction of metal oxides from melting sinter is not easily described, either by laboratory kinetic studies under controlled experimental conditions or by such studies in combination with equilibrium models such as FactSage®. (Its thermodynamic databases relate to the properties of clearly identified solid compounds rather than the variably constituted solid solutions identified as melilite and silicate phases described by van Huyssteen, Harris and Hancock, 1992.)

Lyamina and Shumskii (2003) discuss modelling the kinetics of complex melt reductions of similar composition to lead blast furnace sinters done in conjunction with developing the Kivcet process. In this operation, the high-temperature melt passes through a bed of carboniferous reductant without the influence of additional injected air or oxygen to the system. The model assumes that reduction takes place through a summation of simultaneous independent reactions and diffusion processes involving individual species (see Figure 11). The general equation describing the rate of carbothermic reduction of the individual species can then be stated as:

$$W_i = S[p_{CO}][\mathrm{Me}_i\mathrm{O}]\{A_i \exp(-E_i/\mathrm{RT})\} \tag{10.1}$$

where:

W_i	is the rate of reduction of the ith oxide component (moles s^{-1})
S	is the gas-oxide interfacial surface area (m^2)

p_{CO}	is the partial pressure of CO (atm) at the interfacial surface
$[Me_iO]$	is the molar concentration of the ith oxide component in the melt (mole m^{-3})
$A_i (m\ s^{-1})$, E_i	are the Arrhenius parameters for the ith reduction reaction
T	is the absolute temperature of the melt

The kinetic parameters (A_i and E_i) are determined by the chemical activity of the ith oxide in the melt, which depends on the nature of the given oxide and on the properties of the oxide melt. Lyamina and Shumskii (2003) tabulate values for the Arrhenius terms $\log A_i$ and E_i for various reduction reactions for several synthetic slags in the system PbO–ZnO–FeO–CaO–SiO_2. These data show wide variations in A_i and E_i ascribed to differences in the variation of the CaO/SiO_2 in the experimental melts. The results of generalising the kinetic data obtained over the whole range of melt compositions investigated are plotted on the coordinates $\ln A/T$ and E/RT in Figure 11 from their review paper. Exactly how this was done to eliminate the effects of CaO and SiO_2 contents and their ratio in the experimental slags is not explained, although a cross-reference to the original paper by Sychev *et al* (1977) is cited if the derivation is required. It is assumed that the presentation in Figure 11 now refers to derived A and E/RT values applicable to the reduction kinetics of the pure oxides. In this case, a more useful relationship describing the kinetics of reduction of the individual species might be:

$$W_i = S[p_{CO}](a_{Me_iO})\{A_i \exp(-E_i/RT)\} \qquad (10.2)$$

where:

a_{MeiO} now refers to the thermodynamic activity of the ith oxide calculated from the composition of the melt by a package such as FactSage®, rather than its molar concentration

Solution effects are therefore expressed within a_{MeiO} via the activity coefficient multiplier of the molar concentration, rather than in the kinetic parameters A_i and E_i. In this form, Lyamina and Shumskii's data can be compared with those from later investigations.

The data in Lyamina and Shumskii show a surprising but very consistent outcome over all compositions and for all reduction reactions and diffusion processes in that $\ln A_i/T$ varied directly with E/RT and with the same proportionality factor, as shown in Figure 11. This consistency, described by the authors as a 'compensation effect', was claimed to point to a consistency of the reduction mechanism over the entire range of melt compositions. The results of an appropriately simplified reaction scheme were successfully applied in the modelling of a lead slag reduction scheme for Kivcet reactor design. The authors claim that the experimental results should be applicable to reduction systems other than that of the experiments designed to examine the reduction kinetics in the Kivcet process coke bed (where the molten oxide phase flows in a thin film over reductant carbon). They point out, however, the importance of geometric factors such as the ratio of surface area of the carbon phase to the volume of the slag phase in determining heterogeneous reaction rates appropriate to different reaction systems. In the case of the lead blast furnace, the rate of reduction of PbO and Fe^{3+} in a melt phase by the furnace gas phase at any particular level would require the estimation of values for the interfacial surface S, p_{CO}, [PbO], the activity ratio Fe^{3+}/Fe^{2+} and the solids temperature T in order to use Equation 10.2.

If, rather than a summation of separate individual reactions, the reduction of a melt allows interaction between dissolved species, the term a_{MeiO} is reflective of the CO_2/CO ratio involved in reduction reactions for both lead oxide to metallic lead and for ferric iron to ferrous. It follows that a_{MeiO} is a measure of the oxygen potential of the melt, leading to

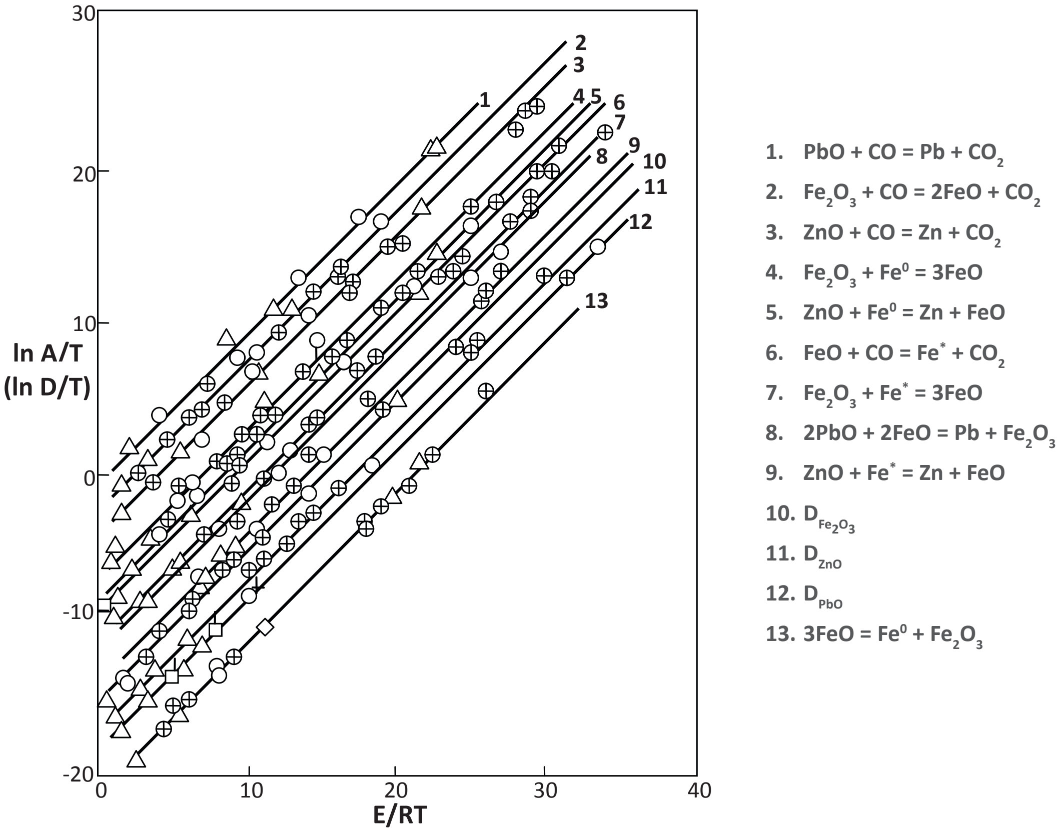

FIG 11 | Relationship between kinetic parameters for reactions and liquid-state diffusion in the carbothermic reduction of oxide melts (Lyamina and Shumskii, 2003). Points – experimental data (Sychev *et al*, 1977).

an equation common to the reduction of both lead and iron species in synthetic zinc-free lead slags cited by Kinaev, Jak and Hayes (2005), which may be expressed as:

$$W_O = S[p_{CO}](a_O)k_O \tag{10.3}$$

where:

W_O	is the rate of removal of oxygen from the melt
S	is the interfacial surface area
a_O	is the activity of reducible oxygen in the melt, measured by the equilibrium CO_2/CO ratio
k_O	is a rate constant representing the contribution of both lead and iron species to the overall reduction rate

Such an equation indicating that a_O applies to all reducible species would support the consistency in the reduction behaviours of the individual melt species shown by Lyamina and Shumskii (2003).

The application of data interpolated from within the range of experimental results, but using a simplified suite of possible reactions, was used for the successful process design modelling of the Kivcet process reduction bed. Reduction behaviour in the field was replicated by the model – a successful empirical outcome, but not necessarily proof of the assumptions originally made in describing the reaction scheme in the laboratory.

Kinaev, Jak and Hayes (2005) investigated the reduction by carbon (with fixed experimental geometry) of zinc-free melts with PbO content varying from 3.1 to 48.0 wt per cent at a fixed SiO_2/CaO ratio of 1.83 and with varying SiO_2/Fe ratios at temperatures from 1423 K to 1573 K. Reduction rate constants for the removal of oxygen (k_O in Equation 10.3, rather than the individual Arrhenius parameters A_i) were determined by exit gas analysis and compared with those for pure PbO. Thermodynamic equilibrium predictions of the oxygen removal associated with the reduction of PbO compared with the total oxygen removal showed that for slags containing between ten and 50 per cent PbO, oxygen removal contributes predominantly to the production of metallic lead. Below five per cent PbO, the proportion of oxygen removed that is associated with the reduction of ferric to ferrous iron increases dramatically with decreasing PbO concentration. An interesting experimental observation in this work was that the exit gas from the overall reaction was effectively in equilibrium with the melt, tentatively explained by the authors as a sequential outcome of reaction between gas and melt following the kinetically controlled reduction reactions in the gas film between the carbon and melt surfaces.

The use by Kinaev, Jak and Hayes (2005) of both equilibrium thermochemistry and reduction kinetics demonstrates a method by which the contribution of individual species to the overall kinetically controlled outcome can be predicted. However, the form of Equation 10.3 is that of a classic Arrhenius equation, which requires that the rate constant increases exponentially with temperature. Figure 11 suggests that, because of the 'compensation effect' inherent in the linear relationships between $\log A_i$ and E_i/RT, the rate of increase in the rate constant is rather less than exponential. Furthermore, equilibrium thermodynamics as applied to reversible reactions postulates the existence of a reverse reaction whose rate at equilibrium exactly equals that of the forward reaction; that is, at equilibrium the net reaction rate is zero. To meet this requirement the driving force for reaction must be defined by the difference between the actual oxygen potential of the melt and the oxygen potential at equilibrium $a(eq)_O$. Equation 10.3 might be better expressed for blast furnace conditions as:

$$W_O = S[p_{CO}][(a_O - a(eq)_O)]k_O \tag{10.4}$$

and Equation 10.2 as:

$$W_i = S[p_{CO}]\left(a_{\mathrm{Me_iO}} - a(eq)_{\mathrm{Me_iO}}\right)\{A_i \exp(-E_i/\mathrm{RT})\} \tag{10.5}$$

In this form, as the melt approaches the equilibrium boundary temperature and composition condition, the reaction rate should slow asymptotically to zero, as foreseen by Lumsden (1960). Equation 10.4, using an experimentally determined k_O, applies only to the zinc-free slags used by Kinaev, Jak and Hayes and should not apply to lead blast furnace conditions (although it is arguably valid for Kivcet coke bed conditions). Equation 10.5 should be of general applicability to the molten reducible blast furnace charge components.

Real problems occur in defining both the melt composition and the reaction surface area as the charge descends through the temperature gradient in the furnace. As a consequence of the changing ratios of melt and residual solids (which can be inferred from the analytical description of Belledune sinters by van Huyssteen, Harris and Hancock, 1992), every term on the right-hand side of Equation 10.5 will vary throughout the composition and temperature gradients of the gas and charge phases.

Changing phase compositions and reduction kinetics

The individual parameters of Equation 10.5 provide a basis for considering reduction kinetics in the lower reduction zone B.

The interfacial surface, S

As discussed, physical measurements of the solid-state surface area of partly reduced sinters (Ward, 1959; Hussain and Morris, 1986) are irrelevant. Measurement of liquid-phase areas at smelting temperatures is not feasible. The assumption used in Kivcet process modelling – that the gas/liquid-phase interfacial surface area can be considered to approximate that of the apparent coke particle surface area (Lyamina and Shumskii, 2003) – is not applicable to lead blast furnace reduction geometry.

In the lead blast furnace, the gas/liquid-phase interfacial surface area S will change as the charge temperature increases. At lower temperatures, say, between 850°C and 1030°C on the evidence of the Chimkent and Belledune experiments, the melt is supported by a lattice of high-melting material within a structure still identifiable with that of the input sinter. With rising temperatures, the supporting material gradually breaks down and becomes incorporated in the melt to form what becomes the slag phase of the equilibrium zone C. The endothermic heat of formation of the slag accompanied by the breakdown of compounds such as the sulfates, spinels and melilites must contribute significantly to the heat balance of reactions in this zone, but the temperatures at which such slagging reactions take place cannot be defined. Lumsden's arbitrary allocation of the thermal contribution of such reactions to other zones of the furnace has now been shown not to accord with observed blast furnace behaviour. What physically happens to the slag after complete fusion is not clear from either the Belledune or Chimkent experiments. The Chimkent description would suggest that the molten slag is still held within the coke bed above tuyere level. In the Belledune case, the molten phase simply disappeared from the sample cage. The progressive change would appear to be undefinable.

Gas phase composition, CO concentration and liquid-phase component activity

In the blast furnace charge, CO reacts with available reducible oxygen at the gas/melt interface to form CO_2 at a rate limited by Equation 10.5 as applying to the reduction of PbO to Pb metal and Fe_2O_3 to Fe_3O_4. It has been shown that it should be possible to predict, from operational performance data, the temperatures and compositions of all phases at the boundary between the upper and lower reduction zones assuming a sinter temperature of 850°C. The term a_{PbO}, which defines the actual oxygen potential of the charge, can therefore also be estimated from the molten phase composition by a recognised method; for example, the FactSage® package cited by Kinaev, Jak and Hayes (2005). The term $a(eq)_{PbO}$ is that of the equilibrium zone end point. The problem is to estimate how the PbO, ZnO and Fe^{3+}/Fe^{2+} contents and ratios in the liquid phase might progressively change as the solid phases melt, the temperature rises and reduction proceeds. All three species in the molten phase are also represented to a significant and variable extent in the gradually melting hardystonite and spinel phases. At the present state-of-the-art level, it is not possible to predict the composition of the molten phase, either from first principles (such as using FactSage®) or by experiment.

Factors affecting the temperature gradient

Lumsden (1960) considered that reduction also takes place by direct reaction of zinc vapour with available oxygen at the interface, with the resultant ZnO product entering the melt. Such a mechanism is also mentioned by Blaskett and Boxall (1990).

It is also possible that Zn vapour diffusing to the interface could react there with reduction product CO_2 to re-form CO and ZnO. Thermochemically, the result is the same and the reducing power of the gas is a summation of the CO and Zn partial pressures. The presence of ZnO in the form of zincite within the ISF sinter charge reported by Holliday, Shoebridge and Firkin (1980) could be supporting evidence for such an idea. On the other hand, the precipitation of solid ZnO might be expected to hinder the penetration of reduction gases into the interior pores of the charge, resulting in a slowing of reaction rates. Hints as to a possible mixed mechanism come from the Chimkent pilot-scale experiment, where Table 1, showing concentrations of zinc species related to the change in lead species concentrations in Figure 6, shows an increase in zinc ferrite roughly corresponding to the decrease in lead ferrite over the temperature range 700–1020°C. At higher temperatures the zinc ferrite concentration decreases as the zinc oxide/silicate fractions increase.

Whatever the mechanism, the oxidation of zinc via the reversion reaction is highly exothermic with the heat of reaction released directly to the charge, tending to raise its temperature, but offset by the endothermic effects of sulfate reduction/decomposition, fusion of high-melting charge components, slag formation, heat of solution of ZnO and heat losses to the jackets and so on. The overall outcome for a given element of vertical height can then be determined by heat balance, always assuming, however, that the rates and temperatures of such supplementary reactions can be established.

The actual definition of the gas composition at the reduction interface is therefore difficult. Lumsden's concept of an overall limitation of the reaction rate by diffusion of the reductant gases to the interface allowed him simply to assume zero concentration of Zn and CO at the interface (although this implied pure PbO at the interface). The concentration gradient from the bulk gas to the interface was thereby accurately defined, and the rate of mass transfer of Zn and CO to the surface and hence the reaction rate could be estimated. This is not the case where reduction is limited by the chemical reaction rate. In light of the finding of Kinaev, Jak and Hayes (2005) that the exit gas in their experiments had a composition approximately in equilibrium with the liquid phase, it might be reasonable to assume such a composition at the interface. The mass transfer rates of gaseous reductants should then equal the calculated reduction rate allowing mass and energy balances to provide an estimate of the change in melt temperature. The problem remains, however, that the composition variation of the liquid phase due to the melting and reduction of sinter components, and hence the oxygen potential of the liquid, must always be conjectural.

A further complicating factor within the temperature range of the lower reduction zone is that of the gasification of the coke by CO_2 in the rising gas phase. This is a net endothermic reaction at the coke surface, the kinetics of which are reasonably well defined for the types of metallurgical coke used in lead smelting. Heat is necessarily transferred from the gas to heat the coke as it descends in the furnace and to supply the endothermic heat of gasification. Whether or not these rates cause a difference in temperature between the coke and bulk gas phase is a point not considered by Lumsden, who merely assumed that heat transfer rates were sufficiently high that the gas, charge and coke temperatures remained roughly the same. On the other hand, the rate of formation of CO by coke gasification will necessarily change the composition of the rising bulk gas phase and must be taken into account in the overall kinetic picture.

Lumsden's calculation of the gas and charge temperature and composition profiles shown in Figure 5 is a much simplified illustrative case where lead reduction persists up to a charge temperature of 1060°C. Lumsden's use of what is, inherently, a very rapid reduction mechanism resulted in a prediction of a rapid evolution of exothermic heat, sufficient to sharply raise the charge temperature as shown in Figure 5, with only a minor effect on the associated gas temperature. Re-examination of his calculations show that this diagram was derived by extension of his calculations for his upper reaction zone models of Figures 3 and 4, ignoring the effects of coke gasification.

If, as has now been shown by experimentation and observation, reduction reactions persist into the lower reduction zone B, possibly right down to the lower boundary with the underlying equilibrium zone, a mathematical description of the thermochemistry becomes much more difficult. Reaction rate control passes from approaching nearly equilibrium conditions at the presumed 1150°C lower boundary to chemical rate control – possibly with some equilibrium influences – at the upper boundary at 850°C. The exothermic reduction reactions now confirmed as taking place in the lower reduction zone provide a much larger input of heat to this zone, still balanced mainly by endothermic coke gasification, sulfate decomposition, slag formation and the raising of charge temperature. Exactly how the respective phase composition and temperature profiles may change is impossible to define, again because of differential rates of melting of variously constituted charge components. From the author's experience with the Lumsden models it might be expected that the lower reduction zone would be upwardly extended before reaching the termination temperatures, first of the gasification reaction at 1000°C and then of liquid silicate reduction at 850°C (that is, the high temperature zones would extend higher in the furnace than predicted by Lumsden).

Evidence of the effect of exothermic reactions in the Chimkent pilot-scale trial is provided by Figure 6, which shows a clear pause in cooling rate in the gas temperature gradient at ~1000°C. Over a height of 1 m in the furnace (20 per cent of the overall burden height) there could have been little physical heat transfer from the gas to the charge, yet the rate of reduction of the lead silicate was at its highest. Figure 5, according to Lumsden, indicates only a slight rise in the gas temperature even if reduction persists to a solids temperature of 1060°C. This is an outcome from assumed elevated reduction rates raising the solids temperature above that of the gases, causing premature fusion of the charge followed by refreezing as PbO reduction slowed and ceased. The Chimkent results merely showed compaction and densification of the sinter in this section of the charge, indicating some softening behaviour but not general fusion followed by refreezing. No solids temperature data measurement was attempted in the Chimkent work. The trial runs were of very limited duration and no constriction of gas flows was reported.

What is certain, however, is that the overall thermal implications of exothermic lead reduction remain but now occur in the lower reduction zone. The exothermic heat of reversion of zinc volatilised in the equilibrium zone must still pass to the furnace contents in the form of sensible heat and also remain as potential heat in the form of unreacted CO in the gases. The physical effects on heat transfer, resultant charge softening and gas permeability can be envisaged but not defined. Thus, the intensity of reaction in the lead blast furnace has unpredictable physical side effects. At this stage of the art, mathematical modelling is virtually impossible in the absence of unequivocal practical data relating to gas and charge composition and temperature profiles.

Modelling of liquid-phase reduction – summary and conclusions

Within the lower reduction zone B, low-melting lead silicates begin to melt and are reduced by the rising gases. At this level in the furnace – say, at temperatures between 850°C and 1030°C – the liquid phase is supported by a lattice of high-melting material within a structure that is still identifiable with that of the input sinter. The coke fraction of the charge is chemically unreactive towards the gas phase. The charge temperature rises as a result of heat transfer from the hotter gases, the exothermic heat of reduction and the exothermic reversion (reoxidation) of residual zinc vapour as the gas temperature falls. The balance between exothermic and endothermic sources leads to a hiatus in the rate of gas-phase temperature rise exemplified in Figure 6.

As the charge descends further and its temperature rises, the supporting material gradually breaks down and becomes incorporated in the melt to form what becomes the discharge slag phase. Reduction reactions of oxidic lead and ferric iron in the molten phases by CO and reversion of zinc vapour provide exothermic heat. Coke begins to react endothermically with the CO_2 content of the gases to form CO at an increasing rate as its temperature rises above 1000°C. The endothermic heat of formation of the slag accompanied by the breakdown of compounds such as the sulfates, spinels and melilites counterbalance the exothermic reactions.

The complex phase structure and constitution of phase components of the reducible charge to the lead blast furnace cannot be determined by readily applicable analytical methods and remain unknown at any point in the furnace. As the sinter passes downwards through the rising temperature gradient within the furnace, the continuously changing fusion temperatures and compositions of the phases in the sinter produce a reducible melt whose composition changes in response to the rise in temperature, reduction by the CO content of the gases and also reaction with zinc vapour in the gases. Reduction reactions and zinc vapour reversion result in thermochemical heat outcomes, which in turn affect the temperature and composition of both gases and charge components. In theory, these thermochemical outcomes can be calculated by the application of known thermodynamic and kinetic principles. In practice, the lack of knowledge of the temperature and phase compositions and their gradients within the operating furnace prevents the development of any reliable mathematical model of reduction in the overall process, although the theory is reasonably well understood.

The consistency of lead blast furnace reduction performance throughout the industry suggests that the reduction rates of oxidic lead are not limiting on the residual lead content of discharge slag. Ignoring the evidence from high-productivity (low residence time) pilot-scale experimentation, it can be concluded that, on industrial-scale furnaces, lead reduction effectively ceases somewhere within the temperature range of the lower reduction zone B. Above the cessation temperature (in the lower part of the lower reduction zone), the thermochemistry becomes that described by Lumsden's furnace reaction zone, illustrated hypothetically for a range of temperatures in Figures 1 and 2. Overall reaction is limited by the gasification of coke by the CO_2 content of the rising gas phase but thermal and chemical equilibrium are maintained between gas and slag phases. The falling gas temperature gradient results in the exothermic reversion of zinc vapour to balance the endothermic gasification reaction. What cannot be established, for lack of an appropriate mathematical model, is the actual cessation temperature of the kinetically controlled reduction of oxidic species.

At lower temperatures in the lower reduction zone B, the outcomes of reaction should be reflected via mass and energy balances by the gradients in the composition and temperature of the charge components and gas phase. Field data should, in theory, provide some direction as to the location and rates of reaction within this zone. Attempts to determine such gradients have failed to provide unambiguous results. Gas-phase temperature measurements have shown significant variation over any horizontal furnace cross-section, with superimposed fluctuation in time. Measurement of the composition of gases containing zinc vapour is not possible for reasons already discussed. There is no practical method for the continuous measurement of the vertical temperature gradients of solid and/or liquid charge components.

What is known is limited to the temperatures and mass flow rates of metallic lead and slag and, by calculation, those of the corresponding gas-phase components under the equilibrium condition prevailing at the lower boundary of the lower reduction zone.

The rate of carbon consumption in the lower reduction zone via the gasification zone can also be established by mass balance using the difference between the total charge input of carbon to the furnace and that associated with the equilibrium discharge products of lead and slag.

The dimensions of water-jacketed lead blast furnaces to achieve reproducible and economically acceptable levels of throughput and recovery of lead in the form of bullion have been well and truly established by empirical development for over a century. The present state-of-art of the lead blast furnace shaft reduction chemistry indicates that changes in practice are more likely to result from a requirement for improved economic or environmental performance than for any revolutionary outcome from laboratory studies, allied with computer modelling of a highly complex and unpredictably variable high-temperature reaction system.

11

On Phase Separation in Lead/Slag Systems

From earlier discussion, it may be concluded that the greater part of the residual lead content of the Port Pirie blast furnace slag is in a metallic form; the remainder is dissolved in the slag in an oxidised form at a concentration determined by the thermochemical properties of the slag/bullion system at the temperature, oxygen and sulfur potentials of the reduction process. Separation of the immiscible liquid lead and slag phases is a topic which, though economically important, seems to have attracted little attention in the technical literature.

Historically, slag was a waste material in which physically entrained and unreduced lead remained in residual quantities, representing an economic loss to the process. The market-based purchase price of concentrate transferred between mine and smelter has traditionally required the smelter to pay for up to 95 per cent of its lead content so that there was always a very considerable economic incentive for the smelter to minimise the amount of lead inevitably lost in dumped slag. The problem was recognised as inherent in the process and early literature reveals consideration of operating and furnace design factors affecting lead recovery such as slag viscosity, physical settling capacity and reduction potential in the furnace. Winterhager and Kammel (1961), following Manson and Segnit (1956), showed that there was a general similarity in slag compositions throughout the industry and reported slag lead content from over 30 lead smelters of that time varying from 0.8 to four per cent. Slag assays also showed varying contents of potentially economically recoverable zinc.

With the advent in the 1930s of the commercial slag-fuming process to recover slag zinc content, it was found that lead as well as zinc was volatilised from the slag, reporting in an oxide fume that could be processed to recover both metals. The discard dump slag following the fuming operation contained only 0.05–0.08 per cent lead, now appreciated as a considerable environmental benefit. The separation of the lead content from the zinc fume and recycling to a lead smelter required either deleading of the zinc oxide by high-temperature volatilisation in a separate process, or precipitation as the sulfate during the leaching stage of electrolytic zinc recovery and reporting in a lead-rich iron-bearing residue sludge. Significant cost penalties were incurred by the lead smelter in treating intermediates from either process so that an incentive remained to minimise losses of lead in slag.

At Port Pirie, after commissioning slag fuming and electrolytic zinc operations in 1967–1968, the recycling of electrolytic zinc plant residue via the sinter plant and blast furnace to recover its lead content presented certain environmental and operating difficulties, including cost penalties, in maintaining sinter output and quality. Interest was therefore in maintaining a low residual lead content in blast furnace slag, but tempered by economic compromises. These were inherent in the effort to maximise zinc production by producing blast furnace slag additional to that required just to produce lead. The integrated operation required recycling of dump slag together with residue to the sinter plant, thus downgrading the lead tenor of the sinter, yet maintaining high lead production rates to satisfy established markets. The effect on residual lead content in slag by increasing the slag production rate through a single, continuous slag-tapping furnace has been mentioned elsewhere in this work. In summary, the residual lead content in slag was shown statistically to rise with an increasing slag production rate, leading to a conclusion that the increase was due to increased entrainment of product metallic lead. Assuming consistent equilibrium conditions at a controlled oxygen potential in the slagging zone, it can be concluded that the dissolved oxide lead percentage should have remained effectively constant. It was difficult to say whether the increase in entrained lead was due to reduced settling time between tuyere and tapping level within the furnace (due to both a design reduction between these levels and increased throughput per unit hearth area) or to a remixing of the slag and bullion phases as they passed together under an underflow weir before reaching the final settling stage in a forehearth.

From the discussion in Section 8, it is clear that the separation of metallic lead during the reduction of sinter in a lead blast furnace proceeds in stages. Firstly, there is the low-temperature release of the metallic lead content produced during the sintering process – in the Port Pirie case, by the practice of adding fine coke to the sinter bed to maintain the oxidised lead content of the product sinter at no more than about 35 per cent. During the updraught sintering process such lead is held within the sinter structure, but much of it can be released by size comminution such as occurs during mechanical handling between the sinter plant and blast furnace, and by attrition within the blast furnace itself. The first stage of chemical reduction in the shaft is that of the small proportion of free PbO and lead ferrite, which has been shown to take place largely from the solid state. The second stage is the liquid-phase reduction of the major lead silicate phases, with the sinter structure maintained by a high-melting lattice of interlocking melilite and spinel crystal phases. Some metal is released to flow directly to the product stream, but the remainder is still held within the lattice structure. The final stage is that where the high-melting crystal phases are absorbed by the formation of a final slag. Coarse metal droplets coalesce into product streams, while final reduction within the slag causes the production of a slag containing previously entrapped metal particles as well as fine particles produced by heterogeneous or homogeneous reduction mechanisms. This ultimate stage occurs deep within the furnace, at temperatures approaching the final tapping temperature, in regions where virtually no experimental investigation techniques are possible. Inference as to what really happens here is necessarily speculative, but physical processes involving sedimentation and coalescence are clearly involved, which in turn depend partly on intrinsic properties of the respective phases such as specific gravity, viscosity and interfacial tension, and partly on physical characteristics of the particular application such as agitation, mixing and interaction with other phases. It may therefore be appropriate to draw analogies with separation technologies other than the lead blast furnace.

Sedimentation

At Port Pirie, a possible definition of slag settling times came via a presentation to the local branch of the AusIMM by one of the many distinguished academic visitors to the BHAS Research and Operating Departments during the 1970s. W G Davenport described some of his early work on metal entrapment in slags which showed that the settling rates of metal droplets in slag could be estimated by a simple application of Stokes' law. Possible mechanisms of generating fine metal droplets were also discussed. Davenport claimed that under turbulent conditions in industrial processes it was entirely probable that fine particles might never effectively separate by sedimentation.

Poggi, Minto and Davenport (1969) showed that under non-turbulent conditions, the rate of spherical droplets settling in various two-liquid systems (including cold models and high-temperature metallurgical systems) followed Stokes' law:

$$V = \frac{2}{9} \frac{g(\rho_D - \rho_s)r_D^2}{\mu_s}$$

where:

V settling velocity (cm sec^{-1})

g gravitational acceleration (cm sec^{-2})

ρ_s density of slag (g cm^{-3})

ρ_D density of droplet (g cm^{-3})

μ_s viscosity of slag (poise)

r_D droplet radius (cm)

For an experimental copper/slag system, the settling time required for 1–10 μm particles to settle 1 cm would vary between three and 300 hours. Poggi, Minto and Davenport claimed that under turbulent conditions, where flows can exist with upward velocities greater than the settling velocity, even large droplets may be prevented from settling. The authors warned that extrapolation of their related experimental results in copper slag/matte systems to industrial conditions was speculative. Nevertheless, the experimental entrapment was of the same order of magnitude as industrial slag losses.

Density

Of the factors in the Stokes' equation, the respective densities of slag and bullion are fixed by the prevailing conditions of the blast furnace, which in turn are dictated by the thermochemistry of the system and are not independently variable. It is somewhat surprising that a concept of phase separation in metallurgical systems is a function only of specific gravity difference and good operating practice seems to have survived in the lead industry even to relatively recent times (for example, Calvo and Ballester, 1986).

Droplet size

With respect to droplet radius, Edwards (1949) showed that the majority of the metallic lead content in granulated Port Pirie slag of that time consisted of some spheres greater than 50 μm radius, but that more than two-thirds of the particles were 15 μm or less. Manson and Segnit (1956) showed an optical micrographic section of a granulated Port Pirie slag with spherical lead prills of 12 and 25 μm radius. Stokes' law calculations yield settling rates of 1.5, 1 and 0.38 h/cm for particles of 12, 15 and 25 μm radius respectively, and 80 sec/cm for a particle of 50 μm. At the time, tapping of the blast furnace slag was intermittent with closure periods up to 15 minutes, providing a rough estimate of the settling time. The tapped slag flowed into a 'settler', which was merely a holding ladle of about 5 t capacity. This was not equipped with weirs, as in a forehearth, and it was quite possible for the slag flow to short circuit to the granulating launder. It would seem that this vessel was not so much a holding basin for the settling of entrained prills of lead, but rather a safety measure in the case of malfunction of the then lead-well siphon, which allowed lead overflow at the slag-tapping level (with consequent real explosion risk in the granulating launder).

Hollitt (1984a) showed a micrographic section of a slag from the later, continuous slag-tapping version of the Port Pirie furnace. This sample had been held at 1200°C for seven hours during a controlled equilibration experiment, then quenched. During this time the total lead content of the sample had decreased from 2.3 per cent to 0.52 per cent, which, because of the careful control of experimental conditions, was considered to have been possible only as a result of the settling out of most of the entrained metallic lead particles. A micrographic section of this slag still showed some prills of 0.6 μm in diameter. The settling rate of such a droplet in a Port Pirie slag is calculated as 56 h/cm.

Viscosity

That the settling velocity of a lead droplet of a given radius is also a function of slag viscosity as well as the difference in specific gravity between metal and slag is strongly supported by the measurements of Manson and Segnit (1956) and Winterhager and Kammel (1961). While the specific gravity difference is probably not subject to much variation from smelter to smelter (although there are few published data on lead slags), viscosity as measured by Winterhager and Kammel for slags from more than 30 different smelters varied in a range from two to ten poise at 1150°C, largely as a result of compositional factors as seen in Figure 12.

The coefficient K_z is determined from the slag composition in mass per cent by a method pioneered by Manson and Segnit (1956) as:

$$K_z = \frac{\%\text{FeO} + \%\text{CaO}}{\%\text{SiO}_2 + \%\text{Al}_2\text{O}_3}$$

where:

%FeO is the molar equivalent of (FeO + ZnO + MnO + MgO)

$\%Al_2O_3$ is the molar equivalent of (Al_2O_3 + Fe_2O_3)

Winterhager and Kammel did not attempt to correlate individual slag viscosities with slag lead content, presumably because of the experimental difficulty of accurately determining the relative contents of metallic and oxidised lead, and because the paper reveals no details of the operating slag temperatures at the different smelters. Nevertheless, the five-fold difference in viscosities is reflected in a roughly five-fold range of slag lead content.

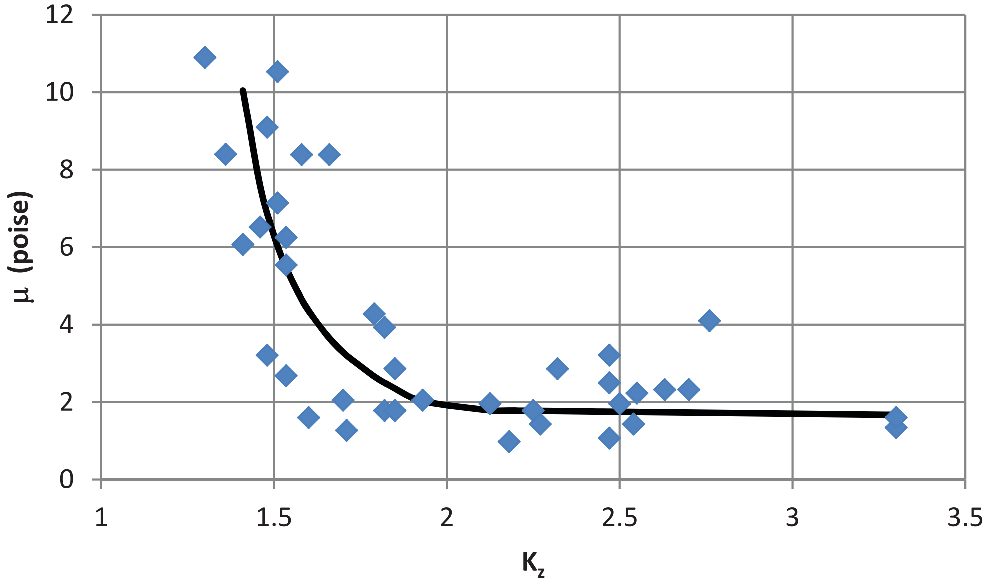

FIG 12 | Lead slag viscosity coefficient at 1150°C. Measured industrial lead blast furnace slag viscosities (Winterhager and Kammel, 1961).

Interfacial tension and coalescence

In a system of two immiscible liquid phases, the two phases will tend to form an interface of minimum area, thus dispersing interfacial energy. Separation of a suspension into larger droplets of the minor phase or the formation of two continuous phases is therefore inevitable. Stable emulsions will form only if the magnitude of the interfacial tension is low or the viscosity of the major phase so high that the rate of coalescence becomes negligible. In general, the stability of an emulsion can be maintained by adding sufficient mixing energy to maintain the interfacial area, or by adding surface active agents to the system to lower the interfacial energy. Where the aim is to encourage phase separation, as in a high-temperature metal-slag system, viscosity again becomes rate-determining. Gentle agitation that enhances collisions between droplets of the minor phase without causing emulsification becomes a means of promoting coalescence of small droplets of the minor phase.

A relevant high-temperature example of phase separation of a lead-rich slag and metallic lead comes from the ancient practice of fire assaying for precious metals (for example, Anderson, 2012). In the scorification stage, an ore sample is fused with fluxes together with a mixture of litharge and a powdered reductant. The objective is to produce a fluid slag phase and metallic lead pellet in which the precious metals are sequestered. The pellet is subsequently treated by cupellation to oxidise the lead, leaving the precious metals in the form of a bead. The art of scorification is to flux the impurities in the sample in such a way that the resultant slag is sufficiently fluid to allow the lead metal to coalesce into the single, freely settling pellet. A viscous slag results in the lead forming small prills of non-settling ‘shot’ in an unsuccessful fusion. The assayer has recourse to a variety of additive remedies to modify the slag viscosity.

An effect of interfacial tension arises in the case where a solid phase is introduced to a two-liquid system. If the interfacial tension between the major phase and the solid is such that one of the liquids ‘wets’ and spreads over the surface of the solid in a thin film, coalescence of this phase is enhanced by the geometry of the system, reducing the distance over which viscosity effects retard separation. If the minor phase preferably wets the solid, the solid becomes a potential means of efficiently separating the two liquids by preferential collection. A particular case of interest to the present discussion is the physical behaviour of molten lead silicates in contact with carbon.

It was shown by Hayes, Okongwu and Toguri (1995) that lead silicates containing 70 per cent PbO and upwards wetted and spread over the surface of glassy carbon and metallurgical coke. As the silica content increased towards silica saturation, the viscosity of the melt increased and the melt became non-wetting, causing significant differences in the reduction mechanism and kinetics. In all cases, however, the carbon surface was assumed to be fully available for reaction either directly with the liquid phase or via an intervening gas phase. Similar wetting and spreading behaviour of lead silicates on ceramics can be inferred from their time-honoured use as glazes.

At higher temperatures, as a lead smelting slag becomes fully formed and fully reduced, it becomes non-wetting towards carbon surfaces. Kinaev, Jak and Hayes (2005) describe a set of circumstances in laboratory studies of slag reduction by solid carbon, where reduction under non-wetting conditions tended to be inhibited by occlusion of the carbon surface by the metallic lead product. This would appear to be a reversal of the situation with high-lead silicates so that now the carbon surface becomes wetted by the lead rather than the slag. Whether or not this observation can be translated to blast furnace conditions is simply not known, but becomes an interesting possibility in understanding phase separation.

System factors

Questions now arise as to how the metallic lead suspension in slag is generated in the blast furnace and whether it is caused or influenced by a particular set of physical and/or chemical conditions.

Poggi, Minto and Davenport (1969) deal specifically with a mechanism of fine droplet formation caused by bubbles of gas rising across a liquid/liquid interface carrying a surface coating of the denser liquid. On rupture of the gas bubble, small droplets of the denser liquid are scattered into the lighter phase. Such droplets can be entrapped as rafts of droplets held on the surface of the lighter liquid, as droplets suspended by small supporting gas bubbles or as fine droplets with extremely low sedimentation rates. Such a mechanism would seem not to apply to reduction in the lead blast furnace where the reducing gas flows past a liquid melt either held within a high-melting remnant crystal lattice from the original sinter, or else at higher temperature flowing over solid coke particles. It may well be relevant to reduction in submerged combustion bath smelting processes for lead such as in the second (reduction) stage of the QSL (Queneau-Schuhmann-Lurgi), Ausmelt or ISASMELT™ processes. Certainly in the early stages of developing these processes, reduction of high-lead slag melts by injecting reducing gas mixtures failed to achieve anticipated results with respect to residual lead in the discharge product. Modern practice using bath smelting methods now tends towards using a blast furnace for the second reduction stage rather than submerged combustion of a reductant in a highly turbulent bath (Errington *et al*, 2005).

Experimental evidence discussed in Sections 8 and 10 shows that while some reduction takes place from the solid state high in the furnace, the major part of the reduction of the oxidised lead fraction of sinter is from a low-melting silicate phase supported in a high-melting crystal lattice. At higher temperatures, when the high-melting components are absorbed into the slag phase, liquid-phase reduction continues towards an equilibrium outcome as the slag flows over and through a predominantly coke bed. Kinetic studies suggest a mechanism of surface reduction of the lead-bearing liquid phase by CO at the gas-liquid interface. The kinetics of reduction of PbO to Pb are heavily favoured by a low energy of activation compared with that of Fe^{3+} to Fe^{2+}. It would seem possible that extremely small droplets of lead formed by surface reduction might be held in place on the gas/slag interface by surface tension forces as discussed by Poggi, Minto and Davenport. A more likely mechanism of retention, however, would seem to be entrapment of metallic product within the still solid crystal lattice structure of the charge as the low-melting liquid phases are reduced.

A second possibility accounting for the formation of fine droplets of metal within the liquid phase is that put forward by Zhao *et al* (2008), who suggest a mechanism for homogeneous reduction based on electrochemical argument. The reaction:

$$O^{2-}(\mathrm{slag}) + CO(g) \rightarrow CO_2(g) + 2e \tag{11.1}$$

takes place at the interface, leading to the subsequent electrochemical reactions:

$$Fe^{3+}(\mathrm{slag}) + e \rightarrow Fe^{2+}(\mathrm{slag}) \tag{11.2}$$

$$Pb^{2+}(\mathrm{slag}) + 2e \rightarrow Pb(l) \tag{11.3}$$

$$Pb^{2+}(\mathrm{slag}) + 2Fe^{2+}(\mathrm{slag}) \rightarrow Pb(l) + 2Fe^{3+}(\mathrm{slag}) \tag{11.4}$$

Suggesting the overall reaction:

$$\mathrm{PbO(slag) + 2FeO(slag) = Pb(l) + Fe_2O_3(slag)} \quad (11.5)$$

This can contribute to overall reduction without requiring direct contact between PbO in slag and the gas-phase reductant. Such a mechanism of homogeneous reduction takes place at a molecular level throughout the liquid phase, thus requiring a presumably viscosity-limited coalescence of the lead into droplets of potentially separable size.

The paper by Zhao *et al* (2008) was not intended to be an examination of metal retention in reduced slag. Rather, it was a laboratory comparison of mechanisms of reduction by CO of alternative blast furnace feeds; namely, sinter and ISASMELT™ first-stage slag. Isothermal reduction of sinter and slag samples was carried out for a fixed period of 30 minutes at 100°C temperature intervals from 800–1100°C. Among other things, these experiments yielded micrographs showing comparative crystal structures of the sinter and slag at increasing degrees of reduction. Such experiments, however, cannot replicate the dynamics of progressive reduction within the temperature and oxygen potential gradients of a blast furnace charge column. Nevertheless, the micrographs are of some relevance to the question of the retention of bullion droplets within crystal structures shown to persist even at the highest experimental temperature of 1100°C. For the sinter specimens, microstructures exhibited increasing porosity created by reduction at lower temperatures, disappearing as molten phases became dominant at 1100°C. All micrographs show blebs of lead about 20 μm in diameter trapped in the melilite framework structure that still remained at 1100°C. Some lead silicate remained at 1100°C, but the space between melilite crystals, occupied by a glassy slag phase containing spinel crystals, showed no sign of metallic lead retention as a separate phase. For the ISASMELT™ slag, the micrographs show no interlocking melilite structures even in the cold unreduced state, while very small zinc spinel crystals (<10 μm) were scattered uniformly throughout the glassy slag matrix. The size of the melilite crystals was related to the rate of cooling during casting of the slag. Softening behaviour occurred 100–150°C below that of a comparable sinter. The authors state that during reduction, metallic lead appeared, scattered throughout the bulk of the slag and not just at the surface of the dense lump sample. In the micrographs, such lead appears as largish globules at least 50 μm in diameter. Although there was no supporting crystal lattice, liquid slag was retained in the sample, a fact attributed to an increase in liquid slag viscosity as PbO was removed by reduction. If the metallic lead globules were produced by the redox mechanism implied by Equation 11.5, some mechanism must be proposed to explain the coalescence of the metal phase formed by homogeneous reaction within the slag.

Field evidence as to the mechanism of phase separation and metal coalescence within partly reduced molten sinter is furnished by textual descriptions of progressive sinter reduction in the Belledune blast furnace (Morris *et al*, 1983). In the region from 3 m down to 2 m above tuyere level (temperatures 850–1050°C), the metallic lead product of liquid-phase reduction was held within the sinter structure, as indicated by a constant total lead content (Table 1). Grains of lead metal had appeared, associated with the lead silicates. The context does not make clear whether the metal was located at the grain boundaries of the lead silicate structures or actually held within the silicate phase. The lead particles increased in size from the centre of the sinter sample towards the edges where they had completely replaced the silicate phase. This suggests that reduction largely takes place at the surface of a shrinking core of low-melting liquid silicates within the high-melting lattice structure. Sequential coalescence of the lead product formed at the grain boundary is then merely the result of the inward retreat of the remaining molten silicate surface.

Given the low iron content of lead-calcium silicate grains observed in Belledune sinter by van Huyssteen, Harris and Hancock (1992) – less than one per cent iron measured as FeO compared with the 28–30 per cent total content of the sinter – it seems unlikely that the redox mechanism of reduction of PbO by Fe^{2+} within the silicate melt as suggested has any significance in this temperature range. Once significant slag formation occurs at higher temperatures lower in the furnace the mechanism may change to a redox system involving iron species (Equation 11.5), in which case the generation of fine droplets within the melt may become real. Unfortunately, the experiments by Morris *et al* (1983) yield no evidence in such temperature ranges – molten phases had flowed out of the sample cage below 2 m above the tuyeres, leaving only residual solid material.

Evidence from the Chimkent pilot trials (Polyvyannyi *et al*, 1971) differs in that only part of the metallic lead formed from liquid silicate reduction at higher temperatures is retained within the residual sinter structure. Figure 6, showing lead species analyses based on bulked average samples of charge materials from sequential horizons of the frozen furnace, reveals that while metallic lead formed by solid-state reduction high in the furnace is retained in the sinter, an increasing fraction is assumed (by difference) to report directly to the product as reduction proceeds. Descriptions in the text refer to globules of lead about 2 mm diameter appearing on the surface of the solid charge about 2.5 m above tuyere level, coalescing to small streams of lead at about 2 m. The gas temperature range here was 900 to 1000°C; the solids temperature was not measured. Some compaction of the sinter was noted at the 2.8 m level, and at the 2 m level the sinter was dense and of low porosity. These observations indicate that, at Chimkent, the softening sinter charge was subject to compressive and abrasive forces within an operating blast furnace. The rounding of the coke at these levels was commented on, although not ascribed to any particular physical or chemical phenomena. In the Belledune experiments, by contrast, the comparatively small sinter sample was contained within a robust cage and thus protected from the effects of such forces as it descended with the charge. It is reasonable to assume that the lack of separation of product lead from the sinter in this case is due largely to the absence of compression and abrasion.

A point of interest arising from both studies is that the molten phase at these temperatures consists mainly of lead silicates (van Huyssteen, Harris and Hancock, 1992), which are completely retained within the sinter structure. This suggests that the known wetting characteristic of lead silicates towards ceramic and carbon surfaces is a factor in strongly holding the reducible phase within a stable, although weakened and softened, melilite-spinel lattice structure.

Polyvyannyi *et al* (1971) provide several pages of detailed mineralogical description of changes in the frozen charge in the Chimkent pilot furnace, observed in 60 samples taken from 12 horizons of the furnace (five from each horizon). Because of the high specific smelting rates in these pilot-scale experiments, reduction of lead silicate glasses persisted down to tuyere level and below. By comparison, at Belledune, the lead silicate glasses had disappeared at a level somewhere above the 1 m level (Table 1).

The mineralogy of Chimkent burden samples at each level shows a gradual change from that of sinter at the stockline to that of a slag at below-tuyere level. The time taken to cool the furnace (to 400°C at tuyere level) after freezing by replacing the blast air with nitrogen was about three hours. It is therefore not surprising that the limited number of micrographic illustrations in the paper to demonstrate particular points in the text should show extensive recrystallisation of the non-metallic fraction with the occurrence of somewhat unexpected phases (for example, matte, speiss, metallic copper, metallic iron and so on). The relevance of evidence from such slowly chilled samples to illustrate high-temperature reduction phenomena is therefore questionable (the same criticism could be made of the Belledune samples in Morris *et al*, 1983). A micrograph of a Chimkent sample from about 0.8 m above tuyere level shows a well-preserved glassy lead silicate phase containing lead droplets of 25 μm in diameter; however, this single micrograph is not necessarily representative of average conditions at this level of the furnace. The general description of samples here states:

> *... metallic lead in samples from this horizon was present in quantities up to 15–20 per cent in the form of irregular streams and in the form of droplets of diameter up to 0.5 mm* (Polyvyannyi *et al,* 1971).

Other micrographs show well-crystallised structures, which, by differing from samples high in the furnace, would seem to suggest formation as a result of the relatively slow cooling of the furnace inherent in the experimental procedure. All that can be said is that metallic lead droplets can be entrapped within partly reduced molten glassy lead silicates, but there is no indication as to whether these might be released as the silicate further reduces or is entrapped as residual silicate is taken up in slag formation at higher temperatures. Some but not all of the other micrographs at this level show roughly spherical lead particles entrapped within the crystal structures.

Samples from below the tuyeres still contained up to 15 per cent metallic lead, which was distributed unevenly in the form of isolated droplets and irregular streams. The non-metallics showed a complex crystal structure, indicative of having cooled slowly from a liquid slag and containing precipitated species such as matte and speiss. No evidence, either for or against a redox mechanism of lead reduction via iron species dissolved in a high temperature melt, was forthcoming from the study of product from the slowly cooled furnace.

In summary, circumstantial evidence from experimental programs not specifically designed to address the problem of metal entrainment in lead blast furnace slags suggests that the main cause lies in the entrapment of small blebs of lead derived from the surface reduction of liquid lead silicates within melilite crystal lattice-like structures. Such structures are inherent in the chemistry of lead blast furnace slags and are formed during the sintering process. Such a mechanism does not preclude the possibility of fine-grained metal precipitates forming within the blast furnace slag at high temperatures by homogeneous liquid-phase reaction between lead and iron oxide species, followed by a coalescence to produce droplets of a size separable by sedimentation in the subtuyere zone of the furnace. Coalescence is suggested by the laboratory study of the reduction of ISASMELT™ slag by Zhao *et al* (2008) and further indicated by industrial results, where blast furnace treatment of such slag results in a product containing 1.9 per cent lead (Errington *et al*, 2005). The rates of both sedimentation and coalescence, however, are constrained by viscosity.

The sedimentation rate dependent on viscosity only applies under static conditions or laminar flow within the slag. As a result, it would seem that phase separation by sedimentation within the furnace of the small remnant fraction of metal is likely only within a hypothetical reservoir of slag retained by an intermittent slag-tapping system or by the weir arrangement of a continuous tapping system. Green (1977) mentions debate sometime prior to 1935 as to such a reservoir at Port Pirie. A consequent increase in height of the tuyeres above taphole level from 300 to 600 mm led to a lowering of residual lead levels without resolving the argument, all because of possible confounding with other favourable operational improvements. Conversely, an increase in residual lead levels followed the reduction of this height to 430 mm on converting the furnace to continuous slag tapping in 1964 (Fern and Jones, 1975).

To the extent that viscosity may influence the residual lead content in slag, the main factors affecting viscosity in the slag/lead metal system are the slag composition and temperature. Figure 12 shows the effect of composition on viscosity at a fixed experimental temperature of 1150°C. The change in viscosity with experimental temperature as shown by comprehensive diagrams by Winterhager and Kammel (1961) varied from site to site with no apparent empirical method of calculation. Changing the composition of a slag will also affect the thermodynamic activity of residual PbO dissolved in slag. Lead smelters in general have over the years adopted slag compositions within the narrow range identified by Manson and Segnit (1956) and Winterhager and Kammel (1961). At Port Pirie the main composition variable affecting total residual lead in slag was the lime/silica ratio (Fern and Jones, 1980). Whether this was a viscosity effect relating to the metallic content or a thermodynamic activity effect on the dissolved component was a local topic of some argument. Hollitt (1992) argues it is both.

Phase separation of two liquids in the presence of a solid phase

Low-energy agitation is used in non-metallurgical unit operations for the separation of low- and high-viscosity liquids; for example, in dairying. There are parallels in lead metallurgy, where a rotary furnace technique is widely used in the secondary lead industry for the reduction of alkali slags formed from the smelting of battery oxides. A similar technique employing a short rotary furnace was used for many years in the Port Pirie lead refinery for the reduction of litharge-rich antimonial slags from the then BHAS softening process (Moffatt, 1993).

These slags were fluxed with soda ash and caustic soda refinery drosses and reduced in a two-stage process by reactive carbon in the form of wood charcoal or brown coal char. In the first stage, the amount of carbon was limited to give preferential reduction of lead that separated out and was tapped off. In the second stage, a more rigorous reduction allowed the formation of an antimony-rich lead alloy (with some arsenic), while the majority of the arsenic was fumed off. The point to be made about this process is that the slags in the rotary furnace were extremely viscous – deliberately so to avoid excessive attack on the refractories by the litharge slag (as refractories improved, furnace lining life improved from two to about six months). Yet there was no particular difficulty in getting metal separation from the slag. There was no zone of high shear resulting in homogenisation of melt phases brought about by gas injection; the viscous nature of the slag combined with the furnace rotation allowed good incorporation – churning and mixing of the melt with the carbon – resulting in the separation of the lead phase that was facilitated by a final period of increased rotation speed of the furnace. Since in the first stage, all carbon was eventually consumed by the reduction reaction and the bath was not sufficiently liquid to be subject to separation by centrifugal forces, it can be concluded that separation during the later part of the first stage was enhanced by contact between the wall of the furnace and the melt bath – possibly in the thin film of melt on the wall carried out of and returned to the bath as it rotated at slow speed. Such a film would provide a much shorter sedimentation path for lead droplets than in the main bath. This suggests positive measures such as the presentation of an interactive solid surface to mixed liquid metal and oxide phases to facilitate phase disengagement.

During the 1970s, an alternative method reduction of such antimonial slags via the SiroSmelt process (predecessor of ISASMELT™ and Ausmelt) was investigated at Port Pirie in conjunction with CSIRO. Although laboratory studies suggested it was feasible, pilot-scale tests were unsuccessful. A lead phase did not appear to form, or if it did, it did not separate, suggesting homogenisation of the two-liquid product phases by the high-shear gas injection.

A two-stage Kaldo process at the Boliden works at Rönskär in Sweden was studied by BHAS from about 1980 to 1984 as part of a program to investigate alternative lead smelting technologies (Ward and Smales, 1982). The process operated in two versions, one for the treatment of leady process recycles (Nystedt, 1980), the other for lead concentrates (Petersson and Erickson, 1977). The chemistry of the concentrate version was comparable to other two-stage direct lead smelting processes under development at the time, but differed in that the single reactor operated cyclically as a batch process between a first direct-smelting stage under oxidising conditions and a second carbothermic reduction stage. In the first stage, dried concentrates and/or recycled dusts and fluxes were pneumatically conveyed into the rotating Kaldo (a top-blown rotary converter – TBRC) reactor by oxygen-enriched air through a water-cooled lance to produce lead bullion and a high-lead slag via an autothermal reaction. In the second stage, common to both versions of the process, the leady feed was discontinued and coke breeze reductant fed into the reactor via a second lance. Temperatures were maintained by heat transfer from the gas phase using a third lance as an oil/oxygen burner. Reduction times in the reduction stage to lower the lead content of the melt from 35–50 per cent to the discharge figure of 2.5 per cent were slightly shorter than for the oxidation stage. The Kaldo TBRC rotated at a high speed compared with the Lurgi short rotary furnace at BHAS and could therefore be expected to give good mixing of the coke breeze and melt. The rotation speed was not so high that any significant centrifugal force was imparted to the melt bath, thus precluding any major sedimentation effect on lead droplets within the bath. Reduction was vigorous and effective. Even though the slag was viscous in the interests of refractory preservation, phase disengagement was good. At the end of the batch cycle the slag temperature was raised to 1150°C to facilitate tapping. Compared with the apparent reduction problems of the Ausmelt and ISASMELT™ reduction stage, the agitation of the carbon in contact with the slag in the Kaldo process achieved high reaction rates and effective phase separation. It is not possible retrospectively to separate the effects on phase separation at the carbon-slag interface or repeated thin-film deposition on the walls through the rotation of the furnace.

Expanded settling capacity?

The use of submerged-arc electric furnaces to assist in phase disengagement of metal or matte entrained in slag is well known in the copper and nickel industries. Often referred to as a settling furnace, the usual assumption is that such a furnace provides additional residence time for separation by sedimentation. However, strong upward convective flows of heated slag in the vicinity of the electrodes induce a churning action in the slag, which must also favour a coalescence of droplets of the minor phase. Such convective flows are known in the electric furnace compartment of Kivcet processes for both copper and lead production, and are essential for the transfer of thermal energy throughout a slag bath common to both oxidation and reduction stages. The extent to which they contribute to phase separation does not appear to have been discussed in the voluminous Russian-language literature on the Kivcet processes.

A BHAS delegation to Plovdiv in Bulgaria in 1970 observed a small electric furnace providing holding capacity between a blast furnace and slag fuming plant. While this was principally a means of marrying the batchwise slag-fuming process to the continuous slag stream from the blast furnace, it also provided some metal-settling capacity.

The use of an electric furnace to boost slag-fuming plant capacity was proposed at Port Pirie during the early 1970s. This was argued as a means of remelting zinc-rich dump slag to feed molten slag on demand to the fuming furnaces. Fuming capacity would have been increased thereby and the thermal requirement for melting would have been supplied electrically at high efficiency compared with recycling through the sinter plant/blast furnace, whose energy source was expensive metallurgical coke necessarily burned under reducing conditions. Recovery of entrained lead was expected but not a major consideration in the overall economics. On the basis of parallel estimates, the insertion of an electric furnace into the sintering/blast furnace train merely to lessen the entrained lead in slag would not have been justified.

While agitation in contact with a solid surface seems to offer a proven means of enhancing phase separation, none of the techniques described here are practically or economically applicable to the slag flow from the lead blast furnace. It is obvious, however, that the slag flow within the furnace must undergo considerable agitation as it passes – from the geometrically undefined point at which it becomes fully formed and fully reduced – towards the taphole and through the solids bed that supports the charge column. This solids bed must consist of residual coke that has failed to burn at tuyere level, probably with some proportion of high-melting sulfidic accretions. Since no coke escapes from the furnace, it must exist in sizes ranging down to zero so that the bed would tend to be closely packed. A picture is then formed of slag trickling through and over such a bed with repeated contact with the solid surface, rather than as discrete rivulets. Such a system should provide favourable conditions for reasonably good phase separation, which is the general case in lead smelting practice. As with any packed bed process, however, good separation has kinetic connotations so that bed depth and throughput are real factors, as has been shown in the various hearth designs at Port Pirie.

In summary, the evidence suggests that the major cause of inadequate phase separation in the lead blast furnace is caused by entrapment of reduced lead within the high-melting crystal lattice inherent in feed material deriving from the sintering process.

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