GASEOUS REDUCTION OF ISASMELT LEAD SLAG AND LEAD BLAST FURNACE SINTERS

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ABSTRACT

Primary lead production using the lead blast furnace in conventional practice is carried out using sinter feed. At YMG, China, the sinter plant has been replaced with a lead ISASMELT furnace. The ISASMELT furnace produces lead bullion plus a high-lead slag, which is cast into lumps to provide a suitable feed for the blast furnace.

In the present study the relative microstructures and reduction characteristics of industrial lead sinters and synthetic ISASMELT slag in CO/CO\(_2\) gas mixtures have been measured and compared. The microstructure and property changes, and the mechanisms of reduction in each case are examined and discussed. The results of the study are used to explain the successful implementation of cast slag feed in commercial ISASMELT- lead blast furnace practice.

Key words: lead slag, lead sinter, lead blast furnace, reduction kinetics and mechanisms

1. INTRODUCTION

The lead blast furnace is still the predominant technology used in the production of primary lead metal [1]. For most operations the feed to the furnace is in the form of oxidized lead sinter produced from lead sulphide concentrates. The sinter plant has the disadvantage that it produces a high volume of low-SO\(_2\) offgas and its mechanical complexity makes it difficult to enclose to eliminate fugitive emissions to the atmosphere. At the YMG plant at Qujing, Yunnan province, China, the oxidation of S to SO\(_2\) is moved from the sinter plant to the ISASMELT furnace [2]. Compared with a sinter plant, the ISASMELT furnace has the advantage that it is readily enclosed and produces a significant quantity of direct lead bullion as well as a high-lead slag suitable for feeding to a blast furnace. In addition the furnace produces a relatively low volume offgas, enriched in SO\(_2\), which reduces the capital cost of the associated sulphuric acid plant.

The physical characteristics of sinter and slag materials are quite different. Sinters are porous, partially-fused agglomerates of variable size, shape and extent of fusion. Cast lead slags are dense, regular in shape and completely fused. Although the cast slag technology has been successfully implemented in industrial practice relatively little has been reported in the open literature about the relative properties and performance of these materials. The aim of the present study is to examine the relative reduction characteristics of sinter and cast slag, and to explain some of the features that enable the cast slag feed to be used in lead blast furnace technology.
2. RESULTS AND DISCUSSIONS

2.1. Reduction rates of lead sinters and slags

In a previous study by the authors [3] preliminary reduction experiments in carbon crucibles were carried out using plant lead sinter and synthetic slag samples. The results of experiments on the reduction of lead sinters and slags in carbon crucibles in temperature range of 800 to 1200 °C were reported. The reduction of industrial lead sinter and synthetic slags with carbon shows that

- below 1000 °C significant reduction of sinter occurs and there is no significant reduction of the slag
- above 1000 °C the rates of reduction in both slag and sinter increase rapidly with increasing temperature.

To more closely reproduce the conditions present in the lead blast furnace shaft the experiments have been extended in the present study to include the use of CO gas as reductant in the temperature range of 800 to 1200 °C. Sinter and slag lump have been used for reduction experiments in CO gas. The samples were cut into single cubes each about 5 grams and placed individually in a molybdenum basket in the reaction tube. The experiments were carried out in a resistance furnace with 30mm ID alumina reaction tube. A Pt/Pt-13%Rh thermocouple was used to monitor temperature. Air was initially flushed from the reaction tube using high purity argon gas. When the sample was raised into the hot zone the gas flow was rapidly switched from argon to CO gas. 200 ml/min sample was quenched into water. The sample and basket were carefully weighed before and after the experiment so that weight loss of the sample can be accurately determined. The compositions of the samples used for reduction experiments in CO gas are given in Table 1 (iron is always present in both ferric and ferrous forms, and was recalculated to Fe₂O₃ for presentation purposes).

Table 1. Bulk compositions of the initial samples used for reduction experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (wt%)</th>
<th>Theoretical max. weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe₂O₃</td>
<td>ZnO</td>
</tr>
<tr>
<td>I8</td>
<td>16.1</td>
<td>9.1</td>
</tr>
<tr>
<td>NP1</td>
<td>21.7</td>
<td>6.6</td>
</tr>
<tr>
<td>PP5</td>
<td>13.5</td>
<td>11.1</td>
</tr>
<tr>
<td>MIMPT15</td>
<td>16.7</td>
<td>11.6</td>
</tr>
<tr>
<td>MIMPT7</td>
<td>17.2</td>
<td>11.5</td>
</tr>
</tbody>
</table>

The samples I8, NP1 are PP5 are typical lead sinters from Mt Isa, Noranda and Port Pirie respectively. The Mt Isa sinter is characterized by high CaO/SiO₂, whereas the CaO/SiO₂ ratio in the Port Pirie sample is typical of the majority of sinter feed materials used commercially [1]. MIMPT15 is a synthetic lead slag that has approximately the same PbO concentration and CaO/SiO₂ ratio as I8. Sample MIMPT7 is intended to
illustrate the behaviour of slags at low CaO/SiO\textsubscript{2} ratio.

Possible reactions between individual components of the sinter/slag and CO gas include:

\begin{align*}
\text{PbO} + \text{CO} & \rightarrow \text{Pb} (\text{liq}) + \text{CO}_2 (\text{gas}) \quad (1) \\
\text{Fe}_2\text{O}_3 + \text{CO} & \rightarrow 2\text{FeO} + \text{CO}_2 (\text{gas}) \quad (2) \\
\text{ZnO} + \text{CO} & \rightarrow \text{Zn} (\text{gas}) + \text{CO}_2 (\text{gas}) \quad (3) \\
\text{FeO} + \text{CO} & \rightarrow \text{Fe} + \text{CO}_2 (\text{gas}) \quad (4) \\
\text{Pb} (\text{liq}) & \rightarrow \text{Pb} (\text{gas}) \quad (5)
\end{align*}

In Table 1 the maximum weight losses are also given assuring the reduction reactions are completed. If only reactions (1) and (2) occur and progress to completion the maximum weight losses for the samples tested are in the range of 5.5-6 wt\% (see Table 1). If reduction of ZnO [reaction (3)] is included the maximum weight losses are in the range fro* 12.6 to 17.2 wt\%.

The equilibrium relative extents of these reactions were assessed using thermodynamic computer modeling package FactSage with the thermodynamic database developed by the authors [8]. Results of this thermodynamic assessment of this multi-component system with a number of complex solutions are presented in Figure 1. In this figure the equilibrium extents of reactions 1 through 5 and resulting oxygen partial pressure at 1100°C are plotted as a function of the CO gas volume in Nm\textsuperscript{3} added per 1000g sinter or slag (again, equilibrium conditions were assumed - fully reacted gas in closed system).

It can be seen from Figure 1 that reactions reduction of PbO to Pb (reaction 1) progress first followed by reduction of ferric to ferrous iron oxides (Reaction 2), the latter is only significant when the reduction of PbO to Pb (reaction 1) is almost complete. Reduction of ZnO to Zn gas (reaction 3) becomes significant only after the reduction of PbO to Pb (reaction 1) is completed. Oxygen partial pressure decreases significantly when most of PbO is reduced to Pb (reaction 1 is nearly completed). It can be seen that only at low $P_{O_2}$ (<10\textsuperscript{-13} atm) a metallic iron is formed (reaction 4). Vaporization of Pb metal(reaction 5) is not significant relative to other reactions, but can take place at all conditions.

experimentally determined weight loss for the sinters and slags following reaction at fixed temperatures and times are presented in Figure 2. It can be seen from the figure that at temperatures below 1100 °C weight losses of sinters, i.e., the extents of reduction, are greater than slags. This can be explained by Figure 3 showing that the connected porosities in the sinter lump samples are much higher than those of the synthetic slag. Therefore the surface area available for contact with the gas phase/unit mass of material is greater in the sinter samples. The "P" marked in Figure 3 is the pores of the present in the sample at low temperatures before melting takes place. The reduction of the dense cast synthetic slag, MIMPT7, is seen to become noticeable above approximately 900 °C, and extents of reaction comparable with sinter materials are achieved for both slag samples at 1100 C.

Note that for all samples weight losses at 1200°C exceeded the maximum weight losses calculated from stoichiometry for reactions (1)+(2)+(3) that suggests possible lead
losses due to vaporization.

![Equilibrium extents of the reactions (1) to (5) and P_{O_2} during the reduction by CO gas of MIMPT7 at 1100°C predicted by FactSage](image1)

Figure 1. Equilibrium extents of the reactions (1) to (5) and P_{O_2} during the reduction by CO gas of MIMPT7 at 1100°C predicted by FactSage

![Weight loss of lead sinter and slag samples after reaction in 200 ml/min CO gas for 30 minutes](image2)

Figure 2. Weight loss of lead sinter and slag samples after reaction in 200 ml/min CO gas for 30 minutes
2.2. Microstructural changes in lead sinters and slags

Typical microstructures of unreduced sinter I8 and synthetic slag MIMPT7 are shown in Figure 4. These materials with high CaO/SiO$_2$ are characterised by the presence of plate-like melilite (2CaO.ZnO.2SiO$_2$) crystals (marked M) that, at high volume fractions, form an interconnected 3D network of refractory material that physically supports the structure during heating [3]. Equiaxed crystals of spinel (ZnO.Fe$_2$O$_3$) (marked S) are also formed embedded in a matrix of lead silicate compounds or glassy silicate (marked L since this material becomes liquid first as at temperatures increase).

The phase assemblages of the lead sinter and slag can be explained by a multicomponent phase diagram reported by the authors [4]. Figure 5 shows a pseudo-ternary section ZnO-Fe$_2$O$_3$-(PbO+CaO+SiO$_2$) with CaO/SiO$_2$ ratio of 0.933 and PbO/(CaO+SiO$_2$) ratio of 3.2. The compositions of lead sinters and slags given in Table 1 are shown in the figure. It can be seen that these compositions are all located in spinel (zinc ferrite) and melilite primary phase fields.
Figure 5. Pseudo-ternary phase diagram ZnO-"Fe$_2$O$_3"-(PbO+CaO+SiO$_2$) with CaO/SiO$_2$=0.933 and PbO/(CaO+SiO$_2$)=3.2 in air [4]

Figure 6 shows the typical changes in microstructure occurring on heating sinter I8 in a reducing atmosphere at temperatures from 800 to 1100°C. It can be seen from these back-scattered electron micrographs that at 800°C limited reaction of the sinter has taken place with the appearance of metallic lead (marked Pb) and the simultaneous creation of porosity within the structure. The pores in the microstructure appear as black areas. The extent of reaction clearly increases with increasing reaction temperature. Note that the framework melilite structure is retained up until at least 1100°C.

Examples of the microstructures formed in synthetic slag MIMPT7 after reduction in CO gas are shown in Figure 7. The slag contains (<10 micron) equiaxed primary spinel (ZnO.Fe$_2$O$_3$) crystals and melilite crystals that are formed from the melts during slow cooling. It can be seen that lead metal is clearly present throughout the bulk of the slag, this is not just at the outer surface of the lump samples. Removal of PbO from solution in the slag increases liquid viscosity, this change in property is supported by the observation that the remaining liquid has been retained on cooling to room temperature as a glassy phase. EPMA measurements have confirmed that metallic iron is formed in MIMPT7 after reaction at 1200°C in pure CO.
Figure 6. Examples of microstructures of quenched sinter I8 after reaction for 30 minutes with CO gas

Figure 7. Typical microstructures of quenched slag MIMPT7 after reaction for 30 minutes with CO gas
2.3. Softening temperatures

The softening characteristics of sinter and slow-cooled synthetic slag samples have also been investigated. Cubic slag samples (30mm diameter) were used for softening temperature test. The tests were carried out by displacement measurements caused by applying a fixed load of 235g to a 8mm OD closed-end alumina tube and the heating the samples at a rate of 400 °C per hour. Examples of the repeated softening temperature tests carried on lead sinter and slag samples are given in Figure 8. Volume fractions of the major phases present in lead sinter and slag as a function of temperature are also presented in Figure 8. It was calculated by FactSage and optimised thermodynamic database for the system ZnO-Fe₂O₃-FeO-PbO-CaO-SiO₂ [8]. The weight fractions obtained from the calculations were converted to the volume fractions of the phases assuming: a) the partial molar volume of each component is constant and the same in the liquid and solid phases, and b) no thermal expansion takes place over the range of temperatures examined.

![Softening curve for sinter I8](image1)

![Softening curve for MIMPT7](image2)

![Phase assembles for I8](image3)

![Phase assembles for MIMPT7](image4)

Figure 8. Experimentally determined softening curves and phase assembles calculated by FactSage for lead sinter I8 and slag MIMPT7 in air

It can be seen that softening occurs over a range of temperatures, which correspond to
the appearance and increasing proportion of liquid phase in the samples. There is some sample-to-sample variation of approximately 100°C in the displacement vs temperature curves. These can be attributed, in the case of the industrial sinters, to variations in microstructure of a micro- and meso-scale, since the materials are composed of recycled (return) lump sinter coated and agglomerated with fused fresh feed. The results of the softening temperature test in synthetic slags show that final softening temperatures are in a relative narrow range between 980 and 1020 °C. This variation in softening characteristics can be explained by small changes in microstructure as a result of differences in cooling rate during sample preparation.

Comparison of the temperatures when softening takes place, temperatures where proportion of liquid and high (Figure 8) and weight losses as a function of temperature (Figure 2) indicates that reduction rates increase significantly after the significant amounts of liquid slag are formed.

2.4. Reaction mechanisms

The classical model reaction models invoked to explain the gaseous reduction of granular porous solid materials, such as shrinking core and grain models, consider a series of mass transfer and chemical reaction steps [5]. The mass transfer processes include gas phase mass transfer from the bulk gas to and from the outer surface of the particle, and gas transfer by porous or Knudsen diffusion through pores in the particle that are either originally present in the material or created as a result of decomposition reactions. In addition, mass transfer through the solution phases can influence kinetics significantly. The chemical reactions are considered to occur at the gas/solid or gas/liquid interfaces.

In the case of gaseous reduction of lead sinters with CO or solid carbon these chemical reactions include reactions with chemical components in both solid and liquid phases. In the case of reactions in lead reduction systems under consideration not only are components present in solution in the liquid slag (so that reduction reactions involve diffusion in liquid slag and possible solid solution phases) but importantly these slag systems contain iron. The presence of iron in the form of ferric (Fe$^{3+}$) and ferrous (Fe$^{2+}$) ions has a dramatic effect on the types of chemical reactions that are possible, in particular electrochemical reactions, reactions involving electron transfer need to be taken into consideration [6]. It can be seen that whilst the reaction

$$\text{O}_2^{2-} (\text{slag}) + \text{CO} (\text{gas}) \rightarrow \text{CO}_2 (\text{gas}) + 2e$$  \hspace{1cm} (6)$$

takes place at the gas/liquid interface, subsequent electrochemical reactions such as

$$\text{Fe}^{3+} (\text{slag}) + e \rightarrow \text{Fe}^{2+} (\text{slag})$$  \hspace{1cm} (7)$$

$$\text{Pb}^{2+} (\text{slag}) + 2e \rightarrow \text{Pb} (\text{liq})$$  \hspace{1cm} (8)$$

$$\text{Pb}^{2+} (\text{slag}) + 2\text{Fe}^{2+} (\text{slag}) \rightarrow \text{Pb} (\text{liq}) + 2\text{Fe}^{3+} (\text{slag})$$  \hspace{1cm} (9)$$

can occur within the liquid phase. Thus the production of electrons through the gas/slag reaction enables these electrons to be transmitted through the slag by an electron hopping mechanism, as electrons are transferred between neighbouring Fe$^{3+}$ and Fe$^{2+}$ ions in the slag (reaction) from the vicinity of the gas/slag interface into the bulk...
liquid slag and does not require movements of Fe ions. This phenomenon has been observed in other chemical and quantified through the use of electrical conductivity measurements [7]. Thus the reaction

$$\text{PbO(slag)} + 2\text{FeO(slag)} \rightarrow \text{Pb(liq)} + \text{Fe}_2\text{O}_3\text{(slag)}$$ (10)

becomes significant in its contribution to the overall reduction; the reduction of lead oxide from the liquid is facilitated by a liquid phase reaction. Significantly this does not require direct contact between PbO species in the slag phase and the reductant in the gas phase as in reaction (2). The geometric constraints requiring high gas/solid or gas/liquid interfacial area to achieve high reaction rates are relaxed and dense liquid slag, i.e. material having zero porosity, can be reduced.

In summary then at low temperatures and with conventional porous sinter materials reducibility is enhanced by increased porosity and surface area, at high temperatures reduction through the liquid phase becomes the dominant mechanism in lead sinters and slags. The significance of the liquid phase reduction mechanism is reinforced by the rapid increase in reaction rate with increasing %liquid present. The increase in liquid fraction also leads to softening of the sinters and slags, it can be seen that there is a correlation between softening temperature and overall reducibility as demonstrated by the sample weight loss vs temperature relationships for the various materials, increasing liquid fraction leads to faster reduction rate.

3. IMPLICATIONS FOR INDUSTRIAL PRACTICE

In the ISASMELT/blast furnace practice at YMG the slag from the ISASMELT furnace at approximately 1050°C is cast into cold steel molds to form ingots of approximate dimensions 100×*0 mm. The effect of this is to produce dense solid slag blocks that are used as blast furnace feed. The structure of the slag depends on the cooling rate of the material. Adjacent to the steel mold the cooling rate is rapid and the liquid phase is effectively transformed into a glassy phase, the solids present in the slag at temperature are retained. These effects are readily reproduced in the laboratory studies; Figure 9 shows samples of MIMP17 slag a) rapidly-cooled and b) slow-cooled from 1150°C respectively. It can be seen that the rapidly-cooled sample contains small size melilite and equiaxed primary spinel (zinc ferrite) crystals in a largely glassy matrix. The microstructure of the slow-cooled sample contains not only primary spinel but also large plate-like melilite crystals and a crystallized matrix consisting of Pb-Fe silicates and Ca$_2$SiO$_4$, this clearly indicates that these additional phases formed on cooling of the samples and further grow of the melilite phase. All of these observations are consistent with FactSage predictions of phase equilibria for this slag composition [3] (see Figure 8).

The question is what will happen to rapidly quenched slag on reheating in the furnace? This was answered by examining the microstructures of synthetic slag samples that had been quenched and reheated to temperature. Figure 10 shows examples of MIMPT7 heated to 900, 950, 1000 and 1050°C respectively. The experiments show that the phase assemblages approach those predicted from chemical equilibrium using FactSage thermodynamic databases [3, 8]; clearly the mass transport in the liquid phase, once formed, is sufficient to rapidly facilitate the phase changes from the quenched to the equilibrium structures.
Figure 9. Typical microstructures of MIMPT7 showing a) rapidly cooled region, 
b) slow-cooled region

Figure 10 Typical microstructures of MIMPT7 in air quenched from 
a)950 °C, b) 1000 °C, c) 1050°C and d) 1100°C

Studies of a commercially operating lead blast furnace using conventional sinter feed [9,10] have shown that "no significant reaction takes place at a level in the furnace above about 3m from the tuyeres, at which point the temperature was about 800 °C". This observation is consistent with the findings in the present studies using a number of different sinter materials (Figure 2) in which the degree of reduction of these materials is low below 800 °C.
The combined kinetic and microstructural evidence indicates that the reduction characteristics of the slag are insensitive to casting conditions, and that rapid reduction through the liquid phase occurs at temperatures between 950-1200°C such that there are no major detrimental effects on the reduction performance of the lead blast furnace using the cast slag feed.

There are other issues to be considered in relation to the operation of the lead blast furnace, for example, the heat balance and the temperature profiles within the furnace. The reduction of lead oxide from slag by CO gas is an exothermic reaction. In conventional practice using sinter feedstock with high reducibility will lead to the generation of heat of reaction in the upper part of the furnace in temperature zones between 700-900°C. It is widely accepted that zinc is reduced in the lower part of the furnace and transferred in the gas phase to be condensed/reoxidised in lower temperature regions of the furnace, i.e. in the middle and upper shaft. The point here is that, reduction and vapourisation of zinc are both highly endothermic reactions, placing pressure on the need to provide heat in the lower furnace. If cast lead slag is used rather than sinter the extent of lead reduction is moved to the higher temperatures experienced in the lower part of the furnace; this has the potential to provide additional chemically-generated heat energy in the high temperature region of the furnace where most required and therefore to more efficiently use the fuel in the furnace.

CONCLUSIONS

The kinetics of reduction of commercial lead sinters and synthetic dense slag samples in CO gas have been measured. It has been shown that rapid reduction of dense slag samples occurs at temperatures between 950 and 1200 °C, and that the extent of reduction achieved are equivalent to those achieved with conventional sinters.

Microstructural changes associated with reduction of these materials have also been examined. It has been shown that rapid reduction is associated with increased proportion of liquid phase in both conventional sinter and cast slags. The results indicate that the dominant reaction mechanism in the reduction of these materials at the temperatures encountered in the lower furnace involve a series of electrochemical reactions, key to these being electron transfer in the liquid slag phase between ferric and ferrous iron species.

The study provides further support to the use in commercial practice of cast high lead slag material as feedstock to the lead blast furnace rather than conventional sinter.

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