

# Interfacial Effects in Gaseous Reduction of PbO · SiO<sub>2</sub> Melts

UDAY B. PAL, T. DEB ROY, and G. SIMKOVICH

The reduction of PbO · SiO<sub>2</sub> melts by H<sub>2</sub>-N<sub>2</sub> mixtures was investigated at 1173 K using a thermogravimetric arrangement. Some of the experiments were specially designed to assess the relative magnitudes of reaction rates at slag/gas, slag/refractory, and slag/metal interfaces. Analysis of the rate data revealed that the reaction rates at slag/gas and slag/refractory interfaces were comparable to each other. Reduction did not occur appreciably at the slag/metal interface. The concentration profiles of lead oxide in the partially reduced quenched slag samples were determined by electron microprobe. Significant concentration gradients of PbO existed at the slag/gas and slag/refractory interfaces. The diffusivity values of lead oxide in the slags were evaluated using the concentration profiles and the rate data. Additions of varied amounts of P<sub>2</sub>O<sub>5</sub> to the slag were found to have a retarding effect on the reduction rate, which may be explained by a surface blockage mechanism.

## I. INTRODUCTION

METAL losses in slags as oxides are of frequent occurrence in the extraction and refining of metals. In the manufacture of alloy steels, oxides of valuable metals such as chromium are lost in slags.<sup>1</sup> Metal losses in slags are well documented for nonferrous metals such as tin<sup>2,3,4</sup> and copper.<sup>5</sup> A potentially attractive process for the recovery of valuable metals lost in slags is by the gaseous reduction of the liquid slag. However, despite the high reaction temperature, the rates of reduction of liquid slags are relatively slow, and this is a major problem in the slag reduction process.

Unlike gas/solid and gas/liquid metal reactions, very little information has been published on gas/slag reactions. While our knowledge of gas/slag reaction is far from being complete, it is known that the reaction rates are influenced by several complex factors such as transport of several species, chemical reactions at heterogeneous reaction sites, and the presence of surface active agents. Therefore, the aim of our research work was to investigate the influence of several of these important factors on the rate of reduction with the objective of enhancing the gas/slag reaction rates in the long run. Emphasis was put on the investigation of the roles played by the interfaces (slag/gas, slag/refractory, and slag/metal) in determining the reduction kinetics.

As mentioned earlier, the reduction of liquid slag can occur at several heterogeneous interfaces. Since there is no direct way to isolate the effects of these interfaces, the possibility of reduction occurring at all types of interfaces must be considered.

Apart from the reduction at the gas/slag interface, hydrogen when utilized as the reducing agent can also be transported through the liquid slag to other potential reaction interfaces (slag/metal and slag/refractory). There have been a number of earlier studies dealing with the dissolution and rapid transport of hydrogen in different forms, through liquid slags of different compositions.<sup>8-11</sup> It may also be of interest to note that the diffusivity of hydrogen molecules<sup>12</sup> through fused solid silica at 1273 K is  $1 \times 10^{-5}$  cm<sup>2</sup> per second and that of helium<sup>13</sup> through a silicate melt (80 pct

SiO<sub>2</sub> and 20 pct Na<sub>2</sub>O) is  $2 \times 10^{-4}$  cm<sup>2</sup> per second. The liquid slag that was used was lead silicate (25 pct SiO<sub>2</sub> and 75 pct PbO) with the PbO opening up the silica structure;<sup>14,15,16</sup> hence, a much higher diffusivity of hydrogen through this slag would be anticipated. In view of the foregoing it is evident that reaction interfaces other than the gas/slag interface must also be considered for the interpretation of the experimental results. It will be evident later (see "Results and Discussion") that reduction did occur at the slag/refractory interface.

In this paper the interfacial effects in the gaseous reduction of lead silicate melts are investigated. The effective diffusivity of PbO in the melt is determined from the measured reduction rate and concentration profiles. The role of a surface active agent which does not participate in the gaseous reduction is also examined.

Systematic analysis of the experimental results obtained from complex industrial slags is not straightforward due to lack of thermodynamic and physical property data. Therefore, experiments were conducted utilizing PbO · SiO<sub>2</sub> melts. This system was chosen because it has relatively low liquidus temperatures and because its thermodynamic and physical property data are available.<sup>6,7</sup>

## II. EXPERIMENTAL DETAILS

### A. Slag Homogenization

The slag samples were prepared by mixing pure PbO (grade 99.99 pct) and pure SiO<sub>2</sub> (grade 99.99 pct) in the desired proportions. The slag samples were contained in an alumina crucible (99.8 pct Al<sub>2</sub>O<sub>3</sub>) and homogenized in an inert atmosphere of purified N<sub>2</sub> at 1273 K for 10 hours. Some homogenized slag samples were sectioned, and the concentration profiles of various constituents in the slag were obtained using electron microprobe (Figure 1). The concentration profiles indicate that the slag was well homogenized with respect to PbO and SiO<sub>2</sub>. Although there was some dissolution of Al<sub>2</sub>O<sub>3</sub> (7 pct or less) from crucible into the slag, the concentration profile of Al<sub>2</sub>O<sub>3</sub> indicates that the dissolution was uniform. In addition, X-ray images for Pb, Si, and Al of various parts of the quenched slag further indicate that the slag was homogeneous.

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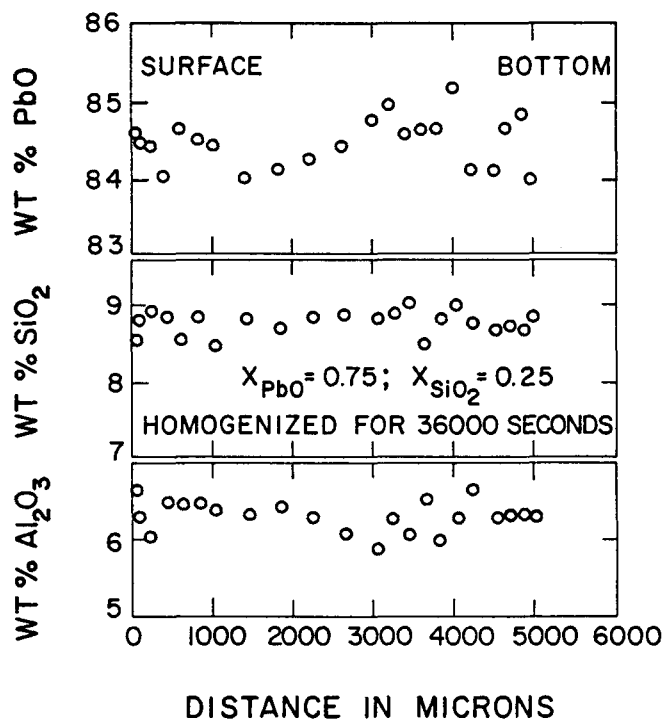


Fig. 1—Distribution of PbO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> in the lead silicate slag homogenized for 10 h at 1273 K.

### B. Thermogravimetric Arrangement

The reduction experiments were carried out in a semi-micro thermogravimetric balance as schematically depicted in Figure 2. An alumina crucible (99.8 pct Al<sub>2</sub>O<sub>3</sub>) containing a known weight of the premelted slag was suspended in a basket in the reaction chamber with a chromel wire. The reaction chamber was heated by a resistance wound Kanthal furnace. The temperature of the hot zone of the furnace was maintained to  $\pm 5$  °C by using a temperature controller. The

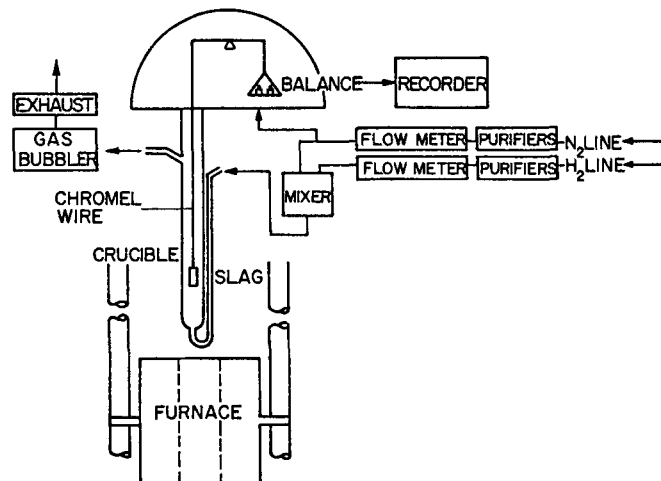


Fig. 2—Thermogravimetric arrangement.

reduction experiments were conducted with different gas flow rates (250 cc/min, 500 cc/min, 1000 cc/min) of H<sub>2</sub>-N<sub>2</sub> mixtures. The reduction rate was found to be independent of the gas flow rate. The gas lines consisted of drierite for removing water, a heated tube containing Cu turnings for the removal of oxygen (from the N<sub>2</sub>), flowmeters, gas mixer, and other accessories as shown in the diagram. The loss of weight during reduction was plotted by a recorder which had a precision of 0.05 mg. The experimental details of various reduction runs are given in Table I.

### C. Analysis of Partially Reduced Quenched Slags

Some of the slag samples were quenched following partial reduction. The cylindrical crucibles containing these quenched slag samples were cut lengthwise using a diamond wheel. The exposed slag surface was then analyzed vertically and horizontally by the electron microprobe to determine the concentration profiles of various constituents

Table I. Details of Various Experimental Runs Using Thermogravimetric Arrangements. Reduction Temperature: 1173 K

S. No.	Initial Slag Weight $\times 10^{-3}$ kg	Initial Slag Composition	Reducing Gas	Purpose
1	8.34	$X_{PbO} = 0.75$ ; $X_{SiO_2} = 0.25$	—	Electron microprobe analysis for homogeneity
2	8.33	$X_{PbO} = 0.75$ ; $X_{SiO_2} = 0.25$	33 pct H <sub>2</sub> -N <sub>2</sub> mix	Electron microprobe analysis (after 480 sec. of reduction)
3	8.32	$X_{PbO} = 0.75$ ; $X_{SiO_2} = 0.25$	33 pct H <sub>2</sub> -N <sub>2</sub> mix	Electron microprobe analysis (after 900 sec. of reduction)
4	8.34	$X_{PbO} = 0.8$ ; $X_{SiO_2} = 0.25$	20 pct H <sub>2</sub> -N <sub>2</sub> mix	Electron microprobe analysis (after 600 sec. of reduction)
5	8.32	$X_{PbO} = 0.75$ ; $X_{SiO_2} = 0.25$	63 pct H <sub>2</sub> -N <sub>2</sub> mix	Note effect with alumina tube immersed
6	8.33	$X_{PbO} = 0.75$ ; $X_{SiO_2} = 0.25$	63 pct H <sub>2</sub> -N <sub>2</sub> mix	-do- (Reproducibility run)
7	8.32	$X_{PbO} = 0.75$ ; $X_{SiO_2} = 0.25$	63 pct H <sub>2</sub> -N <sub>2</sub> mix	Note effect with no alumina tube immersed
8	8.34	$X_{PbO} = 0.75$ ; $X_{SiO_2} = 0.25$	63 pct H <sub>2</sub> -N <sub>2</sub> mix	-do- (reproducibility run)
9	6.65	$X_{PbO} = 0.7$ ; $X_{SiO_2} = 0.3$	63 pct H <sub>2</sub> -N <sub>2</sub> mix	Understand the effect of lead particles
10	6.66	$X_{PbO} = 0.7$ ; $X_{SiO_2} = 0.3$	63 pct H <sub>2</sub> -N <sub>2</sub> mix	-do- (Reproducibility run)
11	8.48	$X_{PbO} = 0.731$ $X_{SiO_2} = 0.244$ ; $X_{P_2O_5} = 0.025$	33 pct H <sub>2</sub> -N <sub>2</sub> mix	Study the effect of P <sub>2</sub> O <sub>5</sub>
12	8.589	$X_{PbO} = 0.73$ ; $X_{SiO_2} = 0.235$ $X_{P_2O_5} = 0.035$	-do-	-do-
13	8.69	$X_{PbO} = 0.72$ ; $X_{SiO_2} = 0.23$ $X_{P_2O_5} = 0.05$	-do-	-do-
14	9.055	$X_{PbO} = 0.68$ ; $X_{SiO_2} = 0.21$ $X_{P_2O_5} = 0.1$	-do-	-do-
15	9.45	$X_{PbO} = 0.64$ ; $X_{SiO_2} = 0.21$ $X_{P_2O_5} = 0.15$	-do-	-do-

(PbO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>). Optical micrographs of the exposed surface of the quenched cut slag samples were also taken.

#### D. Examination of the Role of Interfaces

Three types of experiments were specially designed to study and compare the reaction rates at the slag/gas, slag/refractory, and slag/metal interfaces. Thin walled alumina tubes of known dimension were introduced into a slag of known weight and composition (Table I) so as to create additional slag-refractory interface area without significantly altering the slag/gas interface area. The reduction was carried out in 63 pct H<sub>2</sub>-N<sub>2</sub> mixture at 1173 K in the thermogravimetric balance. After a fractional reduction of about 0.2, the slag was quenched and taken for electron microprobe analysis. In the sectioned slag sample the lead particles were found to be spherical in shape and were present at the top and bottom of the slag. The average lead particle size was estimated and the slag/metal interface area was determined. An identical experiment was conducted without the alumina rod dipped in the slag as a control experiment. The slag composition after a fractional reduction of 0.2 was calculated to be  $X_{\text{PbO}} = 0.7$ ;  $X_{\text{SiO}_2} = 0.3$ . To determine the effect of the lead particles, another slag sample (of initial composition  $X_{\text{PbO}} = 0.7$ ;  $X_{\text{SiO}_2} = 0.3$ ) weighing the same as the former slag reduced to  $X_{\text{PbO}} = 0.7$ ;  $X_{\text{SiO}_2} = 0.3$  was prepared which did not contain lead particles. The reduction of the latter slag (Table I) was also carried out with a 63 pct H<sub>2</sub>-N<sub>2</sub> mixture at 1173 K using the thermogravimetric balance. These sets of experiments were repeated a number of times. Details of the calculations will be presented subsequently.

#### E. Assessment of the Role of P<sub>2</sub>O<sub>5</sub> in the Slag

Different amounts of P<sub>2</sub>O<sub>5</sub> were added to the slag and the slag was homogenized as mentioned earlier (Table I). The reduction experiments were conducted in the thermogravimetric system as discussed earlier. For the purpose of comparison and to note the effect of P<sub>2</sub>O<sub>5</sub> on the reduction rate, all experiments were conducted with 33 pct H<sub>2</sub>-N<sub>2</sub> mixtures at 1173 K.

### III. RESULTS AND DISCUSSION

#### A. Reaction Sites

The slag/gas, slag/refractory, and slag/metal drop interfaces provide potential sites for heterogeneous nucleation of lead and water vapor. The contribution of each of these interfaces to the overall reaction was assessed by conducting several different types of experiments.

Several slag samples were reduced for different extents of time under different reducing conditions (different H<sub>2</sub>/N<sub>2</sub> mixtures) and quenched. These samples were sectioned and an extensive microprobe analysis was conducted to determine the concentration profiles of PbO and SiO<sub>2</sub> both in the horizontal and vertical directions. It may be well to point out that some amount of alumina is soluble in PbO-SiO<sub>2</sub> melts. Therefore, profiles of Al<sub>2</sub>O<sub>3</sub> were also determined together with the profiles of PbO and SiO<sub>2</sub> for these slags both in

the horizontal and vertical directions. It was seen in these concentration profiles that in all cases, gradients of PbO and SiO<sub>2</sub> concentrations existed at the slag/gas and slag/refractory interfaces, although the concentration of alumina was fairly uniform throughout the slag. In Figure 3 a selection of eight such profiles covering the general range of investigation is shown. These concentration profiles (Figure 3) together with the fact that the starting slag was homogeneous (Figure 1) suggests that initially pronounced heterogeneous reaction occurred at the gas/slag and refractory/slag interfaces. This conclusion was also consistent with the optical micrographs of the reduced quenched slag (Figure 4) where lead particles were seen at the slag/gas and slag/refractory interfaces. It may be noted that the presence of metal drops at the slag/refractory interface by itself is not an evidence of reduction occurring at this interface. However, detailed microscopic observation of the slags reduced for a maximum period of 30 minutes revealed the presence of a number of lead particles smaller than a micron in diameter. A straightforward Stokes law calculation showed that the settling time for such small drops through the PbO-SiO<sub>2</sub> melt from gas/slag to slag/refractory interface is in excess of five hours. This, together with the concentration profiles of PbO in the slag reveal the importance of slag/refractory interface in determining the reaction rate. Electron microprobe analysis, however, could not be used to characterize the role of slag/metal drop interface in view of the very small size of the particles. Therefore, to assess the role played by the slag/metal drop interface in determining the overall reduction kinetics, the following three experiments as described earlier were performed. These experiments also allow us to make a comparative estimation of the reaction rates at the slag/gas, slag/refractory, and slag/metal drop interfaces.

*Experiment A:* An alumina tube was dipped in the slag during reaction.

*Experiment B:* Same as the experiment A, but without the alumina tube in the slag.

*Experiment C:* The initial slag composition and weight was the same as the final slag composition and weight after the termination of experiment B. The only difference between the final product of experiment B and the initial material for experiment C was that the latter did not contain any lead particles. The reduction profiles of these three experiments A, B, and C along with their reproducibility runs are shown in Figure 5.

The overall rates of reaction in these experiments are determined by the reaction rates at three different reaction sites. The experimentally determined reaction rates can be represented as the sum of contributions of the surface areas and approximate specific reaction rates at different types of interfaces as follows:

$$R_A = A_1\gamma_1 + A_2\gamma_2 + A_3\gamma_3 \quad [1]$$

$$R_B = A_1\gamma_1 + A_4\gamma_2 + A_3\gamma_3 \quad [2]$$

$$R_C = A_1\gamma_1 + A_4\gamma_2 \quad [3]$$

where  $R_A$ ,  $R_B$ , and  $R_C$  are the measured reaction rates in the experiments A, B, and C, respectively,  $A_1$  is the slag/gas surface area in these experiments,  $A_2$  and  $A_4$  are the

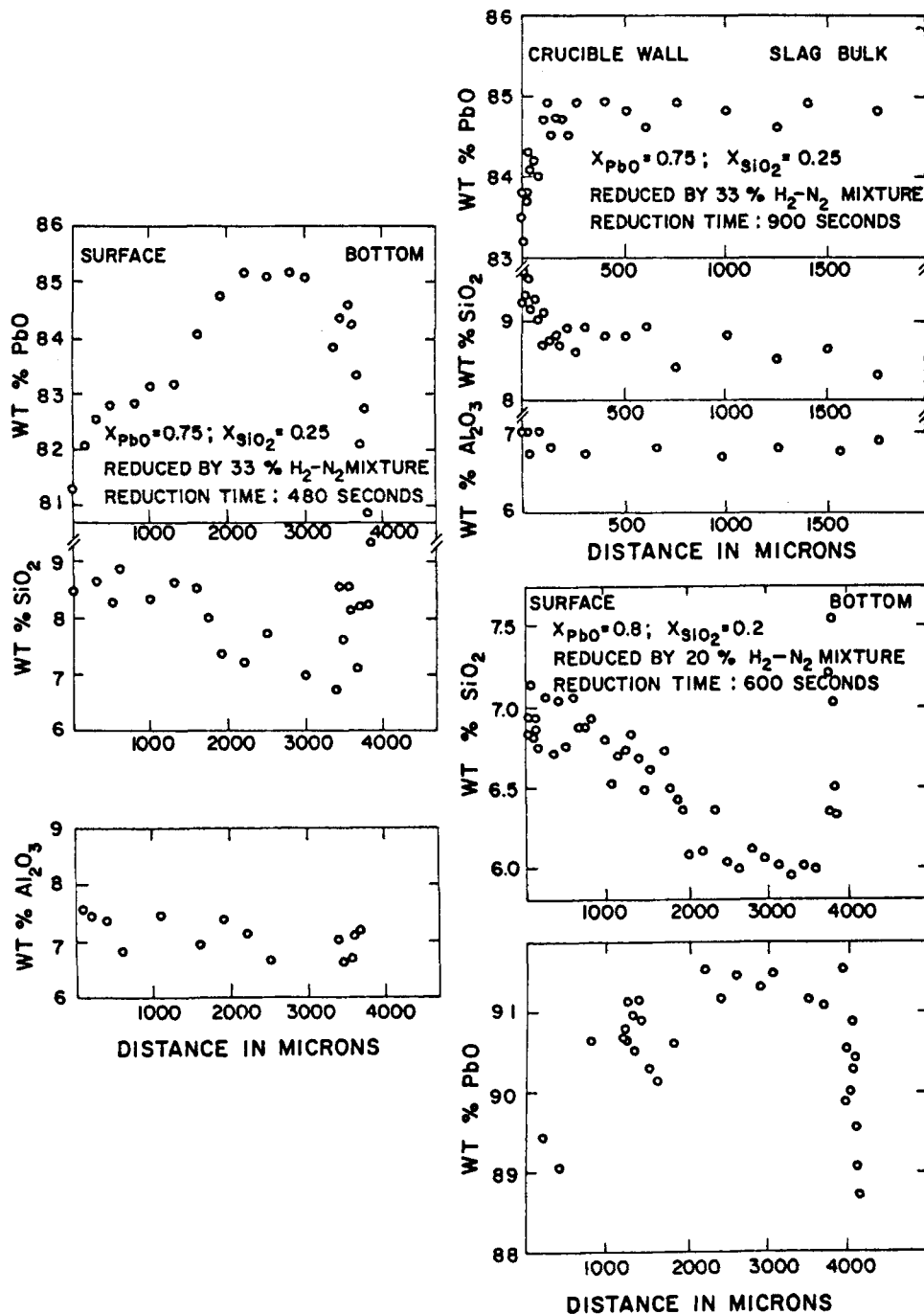


Fig. 3—Profiles of various constituents in 3 different slags reduced by  $H_2-N_2$  mixtures for different extents of time.

slag/refractory surface areas in experiment *A* and in experiments *B* and *C* (same area), respectively,  $A_3$  is the metal surface area in experiments *A* and *B*, and  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$  are the specific reaction rates at slag/gas, slag/refractory, and slag/metal interfaces, respectively.

It is conceivable that the reactants are transported to different reaction sites at the slag/refractory interface at different rates, thereby resulting in a local variation of reaction rate at the interface. Details of such possible variations are not considered in the present analysis. However, the specific reaction rate at the slag/refractory interface used in the

present work represents an average value of the local specific reaction rates. Furthermore, the slag/metal interface area used in the calculation is based on an average particle size of the lead particles which were assumed to be perfect spheres. The average size was determined by optical microscopic examination of the partially reduced quenched slag samples. The values of the specific reaction rates presented in Table II were calculated from the measured values of overall reaction rates for the runs *A*, *B*, and *C*. It is found that the reaction rates at the slag/gas and slag/refractory interfaces are of equal order of magnitude. However, the

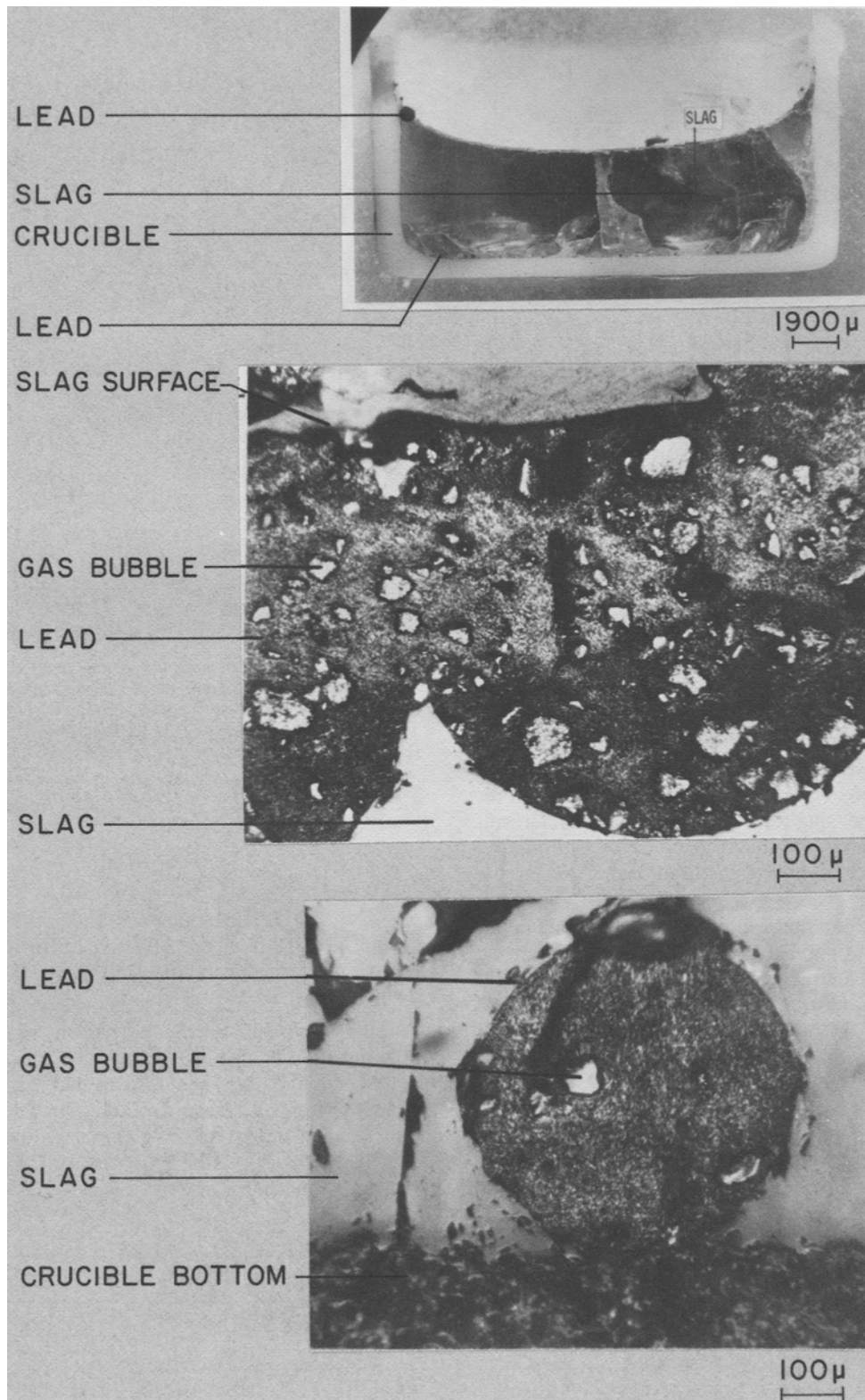


Fig. 4—Optical micrographs of a partially reduced quenched slag sample. Gas bubbles embedded in a matrix of slag and lead at the slag surface and at the crucible bottom.

specific reaction rate at the slag/metal interface is relatively much smaller. The results therefore also indicate that the lead particles do not have any noticeable catalytic action on the reaction rate.

In view of the foregoing conclusions, one may initially hypothesize that hydrogen may be diffusing through the walls of the crucible and reacting with the slag. It is reported that the diffusivity of hydrogen through the sintered alumina

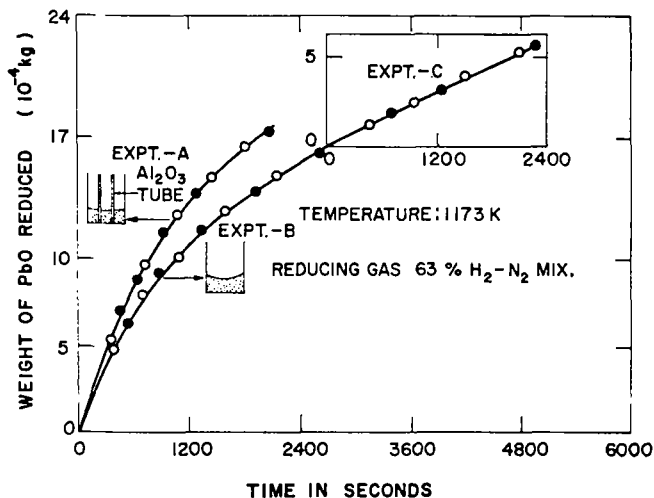


Fig. 5—Weight loss vs time profiles of the experiments conducted to determine the specific reaction rates at slag/gas, slag/refractory, and slag/metal interfaces. Reproducibility runs are indicated by solid dots. Expt. A and Expt. B. Initial slag weight =  $8.3 \times 10^{-3}$  kg. Initial slag composition:  $X_{PbO} = 0.75$ ;  $X_{SiO_2} = 0.25$ . Expt. C. Initial slag weight =  $6.7 \times 10^{-3}$  kg. Initial slag composition:  $X_{PbO} = 0.7$ ;  $X_{SiO_2} = 0.3$ .

is about  $10^{-12}$  m<sup>2</sup> per second at 1200 K.<sup>15</sup> The slags were held in sintered pore free alumina crucible. The reduction time of the slags, partially reduced for electron probe analysis, varied from 300 to 1200 seconds. Hence, the maximum crucible thickness through which the hydrogen can diffuse is approximately  $(\sqrt{Dt}) 3.5 \times 10^{-2}$  mm. However, the crucible that was utilized was about 1.5 mm thick. Therefore, the reduction at the slag/refractory interface as a result of hydrogen diffusing through the crucible is unlikely, leaving the transport of hydrogen through the slag as the only possibility.

The PbO concentration profile as a function of slag depth in experiment A was obtained from the electron microprobe analysis of the reduced quenched slag (Figure 6). Note that at both the gas/slag and refractory/slag interfaces the concentration of PbO was low, indicating again that reduction occurred at or near these interfaces in preference to the bulk slag.

From this profile and the specific reaction rate constants it is possible to calculate an instantaneous effective diffusion coefficient,  $Deff$ , by the use of Fick's first law which is given as

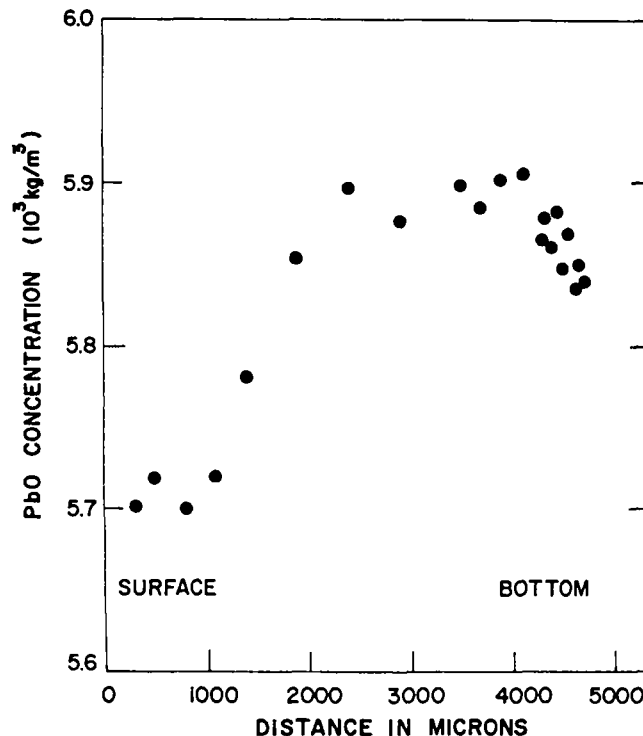


Fig. 6—PbO concentration profile vs slag depth of the experiment conducted with the alumina tube dipped in the slag. Initial slag weight =  $8.3 \times 10^{-3}$  kg. Initial slag composition:  $X_{PbO} = 0.75$ ;  $X_{SiO_2} = 0.25$ . Temperature of reduction = 1173 K. Reducing gas composition: 63 pct H<sub>2</sub>-N<sub>2</sub> mixture.

$$\gamma_i = -Deff \frac{\partial C}{\partial X} \quad [4]$$

where  $\gamma_i$  is the instantaneous flux at the interface  $i$  in  $kg\ m^{-2}\ s^{-1}$ ,  $Deff$  is the effective diffusion coefficient in  $m^2\ s^{-1}$ ,  $C$  is the concentration of PbO in  $kg\ m^{-3}$ , and  $X$  is the distance in m.

Similarly, the  $Deff$  for the experiment without the alumina tube insertion is also calculated. The various parameters in Eq. [4] for the experiments with and without the alumina tube insertion are given in Table III. The  $Deff$  values so obtained are in reasonable agreement with the self diffusion coefficient ( $D_{Pb}^* = 10^{-9.5}$  m<sup>2</sup>/sec) at 1173 K measured by Langanke and Schmalzried.<sup>16</sup>

Table II. Numerical Values of the Interface Areas and the Reaction Rates

	Experiments*		
	A	B	C
Slag-gas surface area ( $10^{-4}$ m <sup>2</sup> )	$A_1 = 2.112$	$A_1 = 2.112$	$A_1 = 2.112$
Slag-refractory surface area ( $10^{-4}$ m <sup>2</sup> )	$A_2 = 6.2$	$A_2 = 4.07$	$A_2 = 4.07$
Slag-metal surface area ( $10^{-4}$ m <sup>2</sup> )	$A_3 = 9.613$	$A_3 = 9.613$	0
Measured overall reaction rates ( $10^{-6}$ kg/sec)	$R_A = 0.4643$	$R_B = 0.3429$	$R_C = 0.3169$
Calculated values of approximate specific reaction rates at different interfaces using the above data:			
slag/refractory interface ( $\gamma_2$ )	$= 0.057 \times 10^{-2}$ kg/m <sup>2</sup> sec		
slag/gas interface ( $\gamma_1$ )	$= 0.0402 \times 10^{-2}$ kg/m <sup>2</sup> sec		
slag/metal interface ( $\gamma_3$ )	$= 0.0027 \times 10^{-2}$ kg/m <sup>2</sup> sec		

\*Each experiment was repeated three times and the average values are presented.

**Table III. Various Parameters Involving Calculation of Diffusivity**

	Expt. with Al <sub>2</sub> O <sub>3</sub> Tube	Expt. without Al <sub>2</sub> O <sub>3</sub> Tube
Time of slag reduction before quenching (sec)	1980	2820
'J' at slag/refractory = $\gamma_2$ (10 <sup>-2</sup> kg/m <sup>2</sup> sec)	0.057	0.057
'J' at slag/gas = $\gamma_1$ (10 <sup>-2</sup> kg/m <sup>2</sup> sec)	0.0402	0.0402
$\partial C/\partial x$ slag/refractory (10 <sup>5</sup> kg/m <sup>4</sup> )	0.9913	1.125
$\partial C/\partial x$ slag/gas (10 <sup>5</sup> kg/m <sup>4</sup> )	0.7575	0.8333
D slag/refractory (m <sup>2</sup> /sec)	5.7 × 10 <sup>-9</sup>	5.1 × 10 <sup>-9</sup>
D slag/gas (m <sup>2</sup> /sec)	5.3 × 10 <sup>-9</sup>	4.8 × 10 <sup>-9</sup>

### B. Effect of P<sub>2</sub>O<sub>5</sub> Addition

Varied amounts of P<sub>2</sub>O<sub>5</sub> were added to the slag of initial composition  $X_{\text{PbO}} = 0.75$  and  $X_{\text{SiO}_2} = 0.25$ , and the reduction experiments were conducted at 1173 K with 33 pct H<sub>2</sub>-N<sub>2</sub> mix. It was seen that P<sub>2</sub>O<sub>5</sub> additions decreased the initial reduction rate of the slag in an asymptotic fashion. The critical mole fraction of P<sub>2</sub>O<sub>5</sub> beyond which the reduction rate remained unaffected was found to be 0.09 (Figure 7). From Caley and Massons work,<sup>17</sup> the activity of P<sub>2</sub>O<sub>5</sub> remained more or less constant (0.003).

It may be noted that under conditions of the present investigation P<sub>2</sub>O<sub>5</sub> can not be reduced to produce P. The standard free energy change  $\Delta G^\circ$  of the reaction  $5\text{PbO} + 2\text{P}(\text{wt pct}) = 5\text{Pb}(l) + \text{P}_2\text{O}_5(l)$  at 1173 K is -37.5 Kcal.<sup>19,20</sup> Now utilizing the reported activity of P<sub>2</sub>O<sub>5</sub> and the reported activity of PbO (0.5)<sup>6,7,17</sup> the equilibrium percentage dissolved phosphorous in metallic lead can be calculated as

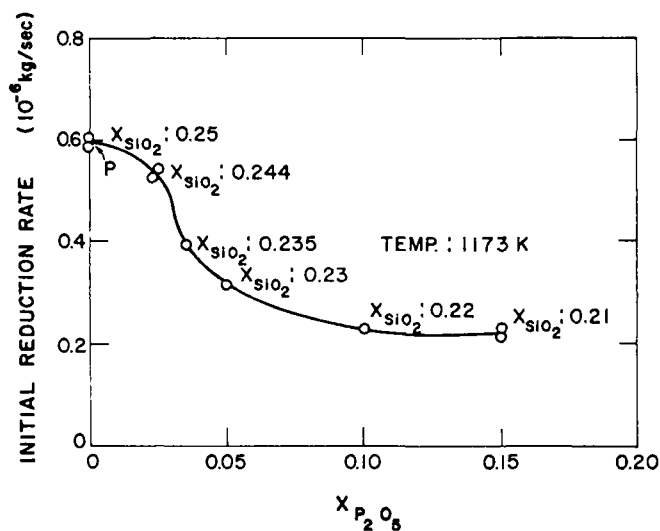


Fig. 7—Initial total reduction rate expressed in the weight of PbO reduced vs mole fraction of P<sub>2</sub>O<sub>5</sub>,  $X_{\text{P}_2\text{O}_5}$ , in the slag. Initial slag weight with no P<sub>2</sub>O<sub>5</sub> = 8.33 × 10<sup>3</sup> kg. Initial slag composition with no P<sub>2</sub>O<sub>5</sub> = 0.75;  $X_{\text{SiO}_2} = 0.25$ . Reducing gas is 33 pct H<sub>2</sub>-N<sub>2</sub> mixture. Reproducibility runs are indicated by 2 points.

pct P = 9 × 10<sup>-5</sup>. This very small value of pct P in liquid metallic lead indicates that practically no phosphorous will be produced. Finally, from the weight loss data recorded by the balance during reduction, the final PbO content of the slag was calculated assuming no P<sub>2</sub>O<sub>5</sub> was reduced. This calculated slag composition agreed relatively well with the quantitative chemical analysis of the reduced slag. Hence, it is apparent that it will be improbable to obtain reduction of any P<sub>2</sub>O<sub>5</sub> under the conditions of the current experiment.

Therefore, the observed decrease in the initial reduction rate with P<sub>2</sub>O<sub>5</sub> additions may be explained by a surface blockage mechanism. It is conceivable that P<sub>2</sub>O<sub>5</sub>, being a surface active species, adsorbs at the slag/gas interface and blocks a fraction of the interface reaction sites. The residual reaction rate observed beyond the critical concentration of P<sub>2</sub>O<sub>5</sub> ( $X_{\text{P}_2\text{O}_5} = 0.09$ ) may be a result of the existence of unoccupied surface sites at apparent surface saturation of P<sub>2</sub>O<sub>5</sub>.

### IV. SUMMARY

The influence of several factors on the kinetics of reduction of PbO-SiO<sub>2</sub> mixtures was investigated at 1173 K. The reaction was found to take place primarily at the slag/gas and slag/refractory interfaces. In contrast, the reaction rate per unit area in the slag/metal interface was much smaller. There were pronounced concentration gradients of PbO at the slag/gas and slag/refractory interfaces. The measured effective diffusivity of lead in the slag was found to be in good agreement with the corresponding independently determined value obtained using a different experimental technique. The reduction rate of the slag was found to decrease in an asymptotic fashion with increasing additions of surface active P<sub>2</sub>O<sub>5</sub>, and this phenomenon can be explained by a surface blockage mechanism.

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