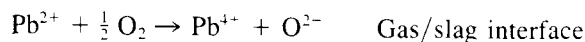# Electronic and Ionic Transport in Liquid PbO-SiO_2 Systems

UDAY PAL, T. DEBROY, and G. SIMKOVICH

The objective of the present work was to examine electronic transport in the PbO-SiO_2 melt. The experimental work consisted of studying the oxidation of liquid Pb covered by a layer of liquid PbO-SiO_2 using a thermogravimetric arrangement. Oxidation of liquid Pb was dependent on the melt height and was parabolic in nature, indicating the oxidation process to be diffusion controlled. We observed a moderate increase in the oxidation rate with additions of a transition metal oxide (Fe_2O_3) to the melt. However, when melt/gas and melt/metal interfaces were short circuited by Ir wires, a much higher increase in the oxidation rate was noticed. Additionally, the conductivity of the PbO-SiO_2 melt with Fe_2O_3 additions was measured as a function of P_{O_2} to detect the nature of electronic contribution by the Fe_2O_3. Combining the results of the oxidation and conductivity experiments, we conclude that the oxidation of liquid lead covered by liquid slag occurs through ionic and rate controlling electronic (probably electron holes) transport in the melt.

I. INTRODUCTION

UNLIKE gas/solid and gas/liquid metal reactions very little information has been published on gas/slag reactions. While our knowledge of gas/slag reactions is far from being complete, it is known that the reaction rates are influenced by several complex factors involving transport of several species and chemical reactions at different reaction sites. Different views have been expressed regarding the transport of oxygen through liquid slag. For instance, Goto[1] has suggested that the physical dissolution of oxygen seems more likely than chemical dissolution in PbO-SiO_2 melts. He argued that oxygen ions do not contribute to the transport of oxygen through the oxide melt as long as there is no electronic conductivity in the melt. The oxygen permeabilities experimentally obtained by Goto were greater by a factor of fifty than the permeability obtained theoretically assuming ionic transport of oxygen anions. Therefore, the major mechanism which supported Goto's results seemed to be the diffusion of physically dissolved oxygen. Caley and Masson[2] investigated the oxidation of liquid lead covered by a layer of PbO-SiO_2 melt. They associated the diffusion of Pb^{4+} with the oxidation of liquid lead underneath the melt and proposed the following interfacial reactions:[2]

$$Pb^{2+} + \tfrac{1}{2} O_2 \rightarrow Pb^{4+} + O^{2-} \quad \text{Gas/slag interface}$$

$$Pb + Pb^{4+} \rightarrow 2Pb^{2+} \quad \text{Slag/metal interface}$$

One of the main difficulties in the study of such reactions is that, due to requirements of electroneutrality, the reactions are generally coupled to other steps in the overall mechanism. Therefore, it is difficult to isolate a single reaction for detailed investigation. For instance, the transport of Pb^{4+} is equivalent to electrons hopping between lead ion sites which is the same as transport of electron holes. Alternatively, the oxidation of liquid lead may also be associated with the counter transport of oxygen ions and electrons. In this paper such possibilities are considered and it is found that the oxidation of liquid lead covered by the melt occurs through counter transport of Pb^{2+} and electron holes.

The work involved measuring the oxidation rates of the liquid Pb covered by slags of different depths. The oxidation measurements were also performed as a function of P_{O_2} and Fe_2O_3 content in the slag. These results were combined with conductivity measurements on the slag to determine the transport mechanism involved in the oxidation of liquid lead. Such an analysis also allowed us to estimate the transport number of electrons in the slag.

II. EXPERIMENTAL DETAILS

A. Oxidation

The oxidation experiments were carried out with N_2/O_2 mixtures in a semi-micro thermogravimetric balance as schematically depicted in Figure 1. An alumina crucible (diameter = 1 cm, height = 2.54 cm) containing known amounts of a slag ($X_{PbO} = 0.55; X_{SiO_2} = 0.45$) and liquid Pb was suspended in the reaction chamber with a platinum wire. The reaction chamber was heated by a SiC furnace. The temperature of the hot zone of the furnace was maintained to ± 1 °C by using a Eurotherm temperature controller. The oxidation experiments were conducted as a function of P_{O_2}, slag depth, and Fe_2O_3 content in the slag. In another type of oxidation experiment Ir wires were inserted through the slag into the metal and the system was exposed to a partial pressure of oxygen equal to 1 atm. The gas lines consisted of drierite for removing water, ascarite for removing CO_2, a heated tube containing Cu for the removal of oxygen (from the N_2), flowmeters, a gas mixer, and other accessories as shown in Figure 1. The weight gain during oxidation was plotted by a recorder with a precision of 0.05 mg. The average duration of the oxidation experiments was about 21 hours.

To determine the height of the slag above the lead, the crucibles were quenched following oxidation and were cut lengthwise along its axis using a diamond wheel. The exposed slag surface area (Figure 2) was measured. The height of the slag was obtained by dividing the measured area by the diameter of the crucible. This was done for all the crucibles used in the oxidation runs.
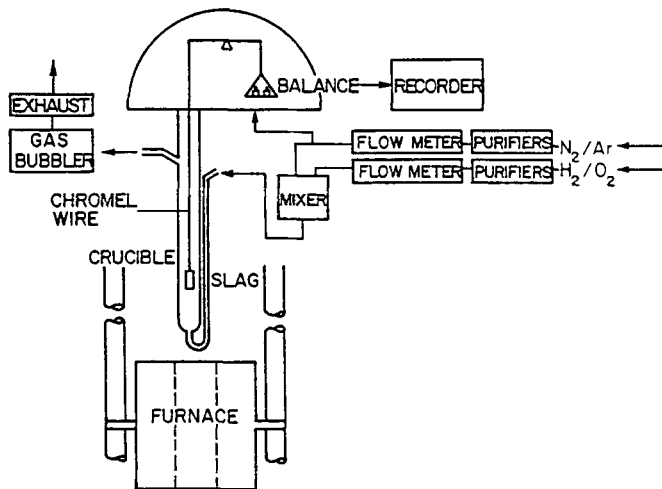
Fig 1—Schematic diagram of the thermogravimetric arrangement for oxidation
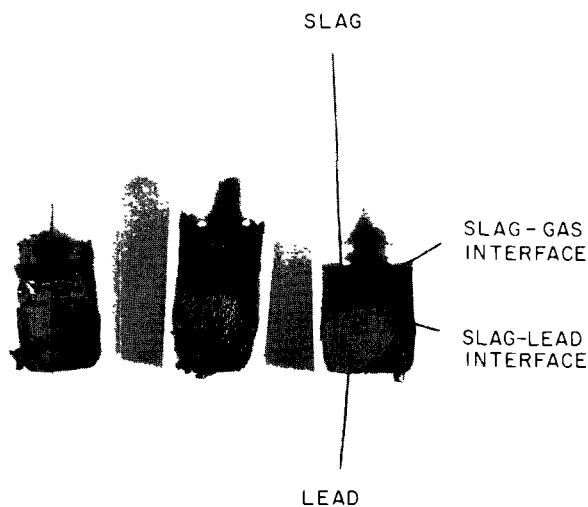
Fig 2—Typical photographs of the shape of slag over the lead

Fig 3—Schematic diagram of the conductivity cell

B. Conductivity Measurements

The cell assembly used to measure the conductivity of the lead silicate system with Fe_2O_3 additions under different environments is shown in Figure 3. The height of the liquid oxide used in the crucible was between 2 to 2.5 mm (calculated from molar volume[3]). The electrodes were made of iridium wire of diameter 1 mm. The connecting wires from the electrodes to the resistance measuring unit were also of Ir but of a smaller diameter (0.25 mm). The cell constant was determined by using 0.01N KCL solution at 24 °C. The conductivity measurements were made with a high frequency ($>10^3$ Hz) General Radio 1658 RLC bridge to avoid polarization of the slag.

The reaction chamber containing the cell assembly was heated by a resistance-wound Kanthal furnace. The temperature of the hot zone of the furnace was maintained to ± 1 °C by using an Omega Model 149 solid state temperature controller. The gas lines used were similar to the ones used for the oxidation experiments. All of the conductivity measurements were mad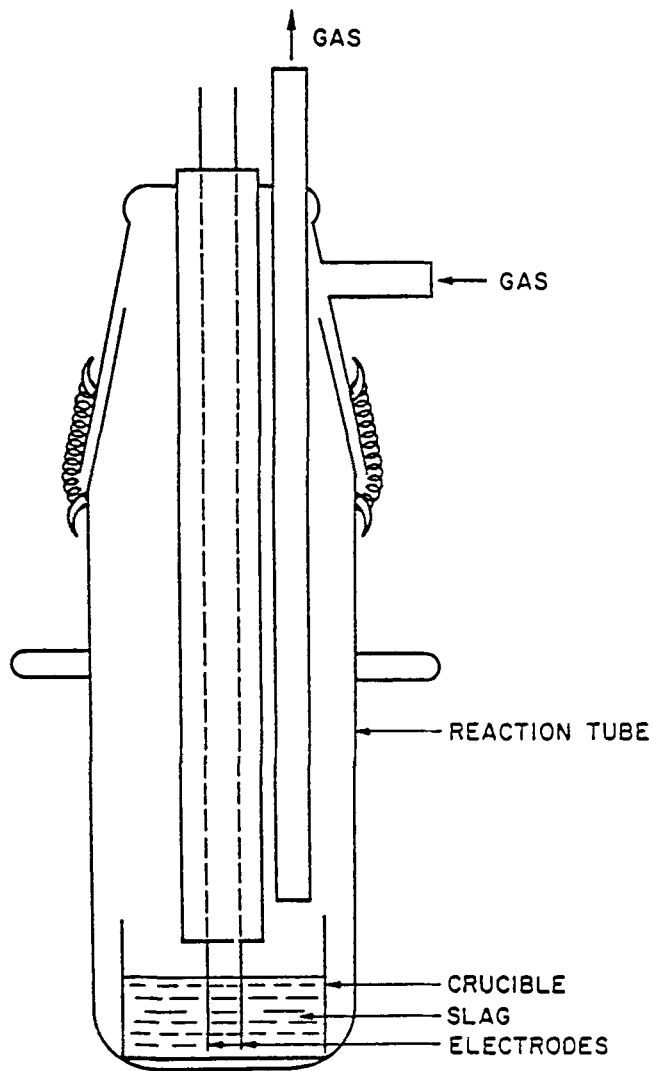e with a total gas flow rate of 835 cc per minute (velocity = 100 cm per minute through the reaction tube). Two series of measurements were made:

(i) Conductivity measurements were made as a function of temperature for slags containing no Fe_2O_3.
(ii) Measurements were made at 1173 K as a function of P_{O_2} for slags containing different amounts of Fe_2O_3.

III. RESULTS AND DISCUSSION

A. Rate Controlling Step

The oxidation of the molten lead was followed as a function of the slag height in oxygen (P_{O_2} = 1 atm) for 21 hours. The oxidation of liquid lead was extremely slow and the slag height above the liquid lead hardly changed during the duration of the experiment. Therefore, for a given slag height, the variation in the oxidation rate of the liquid lead is unnoticeable in 21 hours. The oxidation of Pb for different slag heights in the range of 2.5 mm to 6 mm is shown in Figure 4. The oxidation rate was found to be inversely proportional to the slag height indicating that the oxidation,
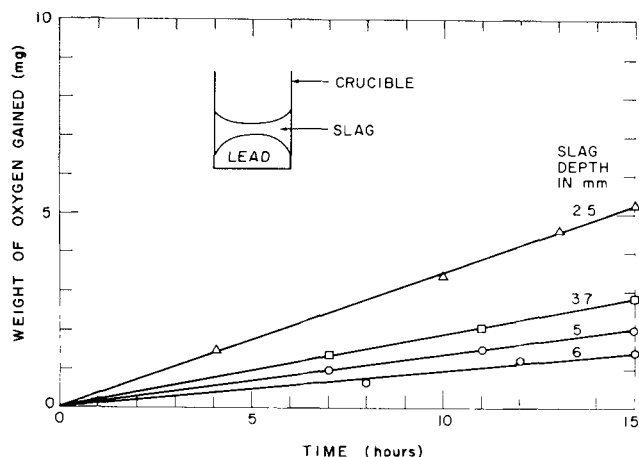
Fig. 4—Oxidation plots for liquid lead covered by liquid slag (55 mole pct PbO; 45 mole pct SiO₂) at 1173 K. $P_{O_2} = 1$ atm
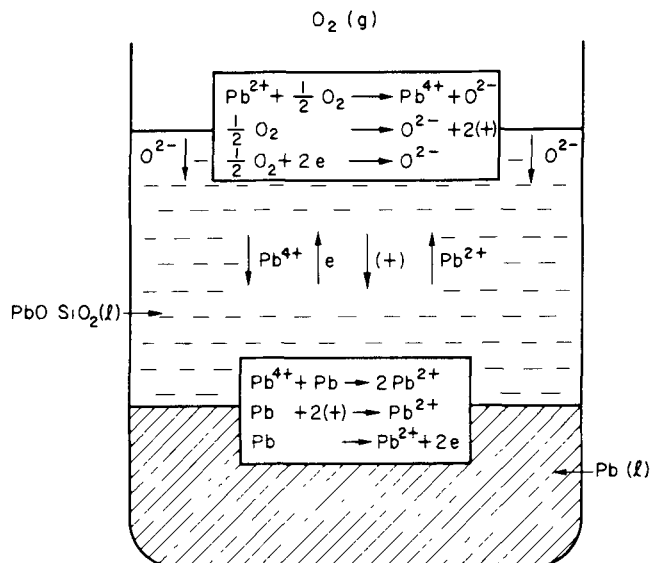

Fig. 5—Conceptual model for the oxidation of liquid Pb underlying a liquid PbO-SiO₂ melt. The formation and motion of the charged silicates is generally ignored in view of the fact that they contribute little to the transport processes that occur

in reality, was parabolic in nature. We can, therefore, write the rate as follows:

$$\frac{1}{A} \cdot \frac{dn}{dt} = \frac{kr}{x} \quad [1]$$

where

dn/dt is the rate of weight gain of oxygen,
x is the slag height over the lead,
kr is the specific rate constant, and
A is the slag metal interface area.

The numerical values of the oxidation rate for different slag heights and the calculated values of specific rate constant kr are presented in Table I.

B. Transport Mechanism

Figuratively, the oxidation may be visualized as consisting of reactions at the slag/gas and slag/metal interfaces and the transport of Pb^{4+}, Pb^{2+}, e, and $(+)$ through the slag layer as depicted in Figure 5. At first we shall show that if we use Wagner's oxidation theory for electronic transport, as suggested by Goto,[1] we arrive at the transport number of electrons as predicted by earlier workers.[1,3,4] Then out of the possible electronic modes of transport we shall show evidence of electron hole (+) motion accompanying ionic transport maintaining electrical neutrality.

1. Electronic transport

The specific rate constant kr can be expressed electrochemically[5] as

$$kr = \frac{RT}{2|Z_2|F^2} \int_{P_{O_2}}^{P'_{O_2}} \frac{(t_1 + t_2)\sigma_\Sigma t_3}{t_1 + t_2 + t_3} \cdot d \ln P_{O_2} \quad [2]$$

where

R is the gas constant
T is the oxidation temperature 1173 K
$|Z_2|$ is the valence of the anion
F is the Faraday constant in cal/equivalent volt

t_1, t_2, t_3 are transport numbers of cations, anions, and electrons (or holes), respectively

σ_Σ is the overall electrical conductivity

P'_{O_2} and P''_{O_2} are the partial pressures of oxygen at the slag/metal and slag/gas interfaces, respectively

P'_{O_2} is the equilibrium value of P_{O_2} between Pb/PbO in the melt ($\sim 10^{-12}$ atm) and $P''_{O_2} = 1$ atm. However, earlier workers[1,3,4,6] have shown that in PbO-SiO₂ melts $(t_1 + t_2) = 1$ and $t_3 \ll 1$. Therefore, Eq. [2] can be further simplified to

$$kr = \frac{RT}{2|Z_2|F^2} \int_{10^{-12}}^{1} \sigma_\Sigma t_3 d \ln P_{O_2} \quad [3]$$

where the P_{O_2}'s have been replaced by their experimental values.

The overall conductivity of the slag ($X_{PbO} = 0.55$; $X_{SiO_2} = 0.45$) σ_Σ was measured as a function of temperature and is shown in Figure 6. The value of σ_Σ at 1173 K from Figure 6 and the value of kr at 1173 K from Table I were used in Eq. [3] to calculate the transport number of electrons ($t_3 = 1.4 \times 10^{-3}$). The maximum transport number

Table I. Numerical Values for Oxidation Rate as a Function of Slag Depth for Slag Containing No Additives. Temperature 1173 K

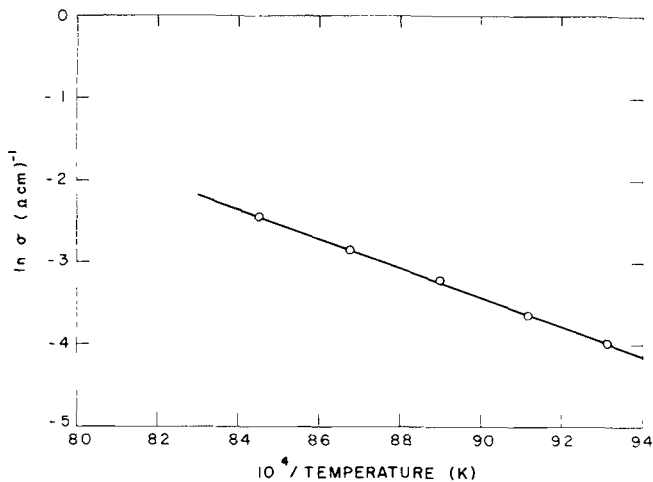| Slag Number	Slag Depth	Oxidation Rate	Kr	P_{O_2}
1	2.5 mm	12.32×10^{-9} equiv/cm²-s	3.08×10^{-9} equiv/cm-s	1 atm
2	2.5 mm	12.4×10^{-9} equiv/cm²-s	3.10×10^{-9} equiv/cm-s	1 atm
3	3.7 mm	7.94×10^{-9} equiv/cm²-s	2.94×10^{-9} equiv/cm-s	1 atm
4	5.0 mm	6.0×10^{-9} equiv/cm²-s	3.00×10^{-9} equiv/cm-s	1 atm
5	6.0 mm	5.14×10^{-9} equiv/cm²-s	3.08×10^{-9} equiv/cm-s	1 atm

Average value of $Kr = 3.04 \times 10^{-9}$ equiv/cm-s

Fig 6—Variation of conductivity as a function of the reciprocal of temperature for a slag of composition 55 mole pct PbO and 45 mole pct SiO₂ P_{O_2} = 0 21 atm
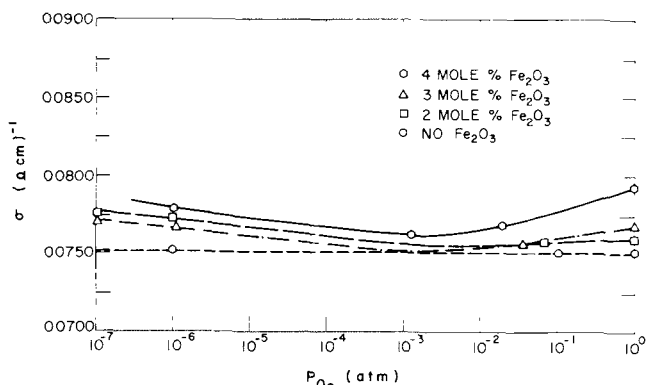

Fig. 7—Conductivity vs partial pressure of oxygen for slags (55 mole pct PbO and 45 mole pct SiO₂) containing different amounts of Fe₂O₃ at 1173 K

of electrons in PbO-SiO₂ melts as predicted by earlier workers[3,4] is of the order of 10^{-3}. Therefore, the value of 't_3' obtained by us is quite reasonable and supports the phenomena of electronic and ionic transport in the melt maintaining electrical neutrality in the transport process.

2. Hole '(+)' transport

In this section electrical conductivity measurements on the slag are combined with the foregoing analysis to find the nature of electronic transport, 'holes or electrons'.

The slag (X_{PbO} = 0.55, X_{SiO_2} = 0.45) showed no detectable variation of conductivity with P_{O_2}. This may, however, be expected in view of the very low concentration of electronic species with low transport numbers (10^{-3}). However, there was a slight increase in the conductivity with increasing additions of Fe₂O₃ to the slag. In contrast to the slag with no Fe₂O₃, the slag with Fe₂O₃ showed some variation in its conductivity as a function of P_{O_2}. The variation of the conductivity of the slag as a function of Fe₂O₃ content and P_{O_2} at 1173 K is shown in Figure 7. From the plot in Figure 7 it can be seen that slags with Fe₂O₃ exhibited n-type behaviors at P_{O_2} values $<10^{-3}$ atm and a p-type behavior at P_{O_2} values $>10^{-3}$ atm.

Oxidation of the molten lead covered with slags (X_{PbO} = 0.55; X_{SiO_2} = 0.45) of different heights containing vary-

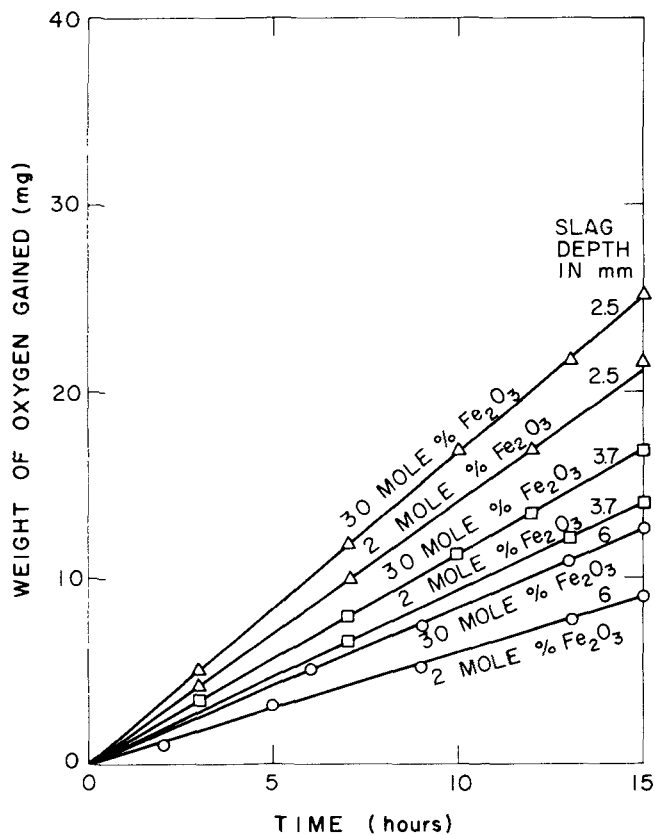Fig 8—Oxidation plots of liquid lead covered by slags (55 mole pct PbO and 45 mole pct SiO₂) containing different amounts of Fe₂O₃ at 1173 K P_{O_2} = 1 atm

ing amounts of Fe₂O₃ was conducted at 1173 K with P_{O_2} = 1 atm. These oxidation plots with varying amounts of Fe₂O₃ in the slag are shown in Figure 8. From Figure 8 it can be said that additions of Fe₂O₃ to the slag increased the oxidation rate of the molten lead. For instance, when 2 mole pct Fe₂O₃ was added to the slag, the oxidation rate increased by five times as compared to the slag with no Fe₂O₃. This indicates that the addition of Fe₂O₃ to the slag at P_{O_2} = 1 atm increases electronic conduction in the slag which increases the oxygen transport through the slag. It is also known that for p-type materials the hole concentration '(+)' decreases and electron concentration '(−)' increases with decrease in P_{O_2}. Oxidation experiments were therefore conducted at P_{O_2} = 0.5 atm with slags containing no Fe₂O₃ and 2 mole pct Fe₂O₃. These oxidation plots at P_{O_2} = 1 atm and P_{O_2} = 0 atm are shown in Figure 9. It is observed that as P_{O_2} is lowered, the oxidation rate decreases due to a decrease in electronic transport. Therefore, the oxidation of liquid lead is directly linked to electronic transport (probably holes) and satisfies the transport mechanism as explained earlier. Conversely, if n-type conduction was rate controlling, then the oxidation rate at these high oxygen pressures would be relatively constant as a function of P_{O_2}.

3. Change in conductivity of the slag with Fe₂O₃ additions

If we assume that small additions of Fe₂O₃ to the slag act only as hole contributors and do not change any other properties of the slag, then Eq. [3] may be modified as:
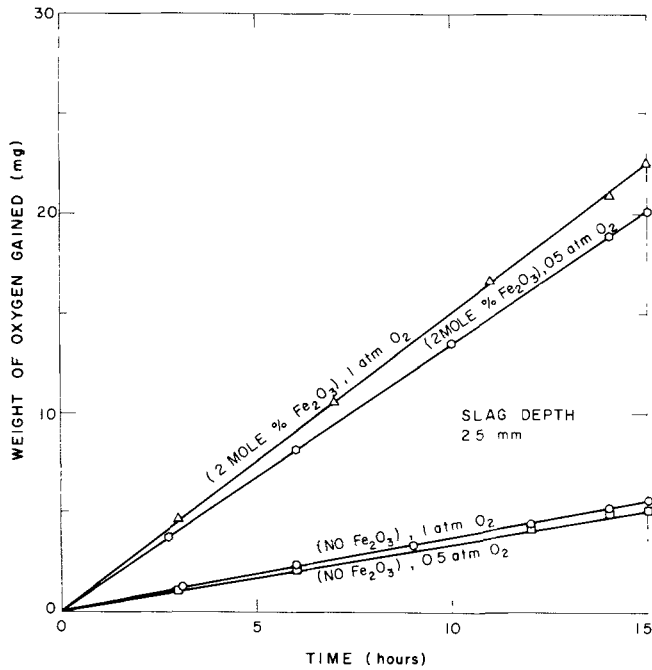
Fig. 9—Oxidation plots of liquid lead covered by slags (55 mole pct PbO and 45 mole pct SiO_2) containing 2 mole pct and 0 mole pct Fe_2O_3 at two different partial pressures of oxygen

$$kr = \frac{RT}{2|Z_2|F^2} \int_{3.12 \times 10^{-12}}^{1} (+)e\mu_3 d \ln P_{O_2} \quad [4]$$

where
(+) is the concentration of holes
e is the electronic charge
μ_3 is the hole mobility.

The concentration of holes '(+)' may be assumed to be directly proportional to the concentration of Fe_2O_3 for low concentrations. Thus,

$$(+) = kn_3 \quad [5]$$

where n_3 is the mole fraction of Fe_2O_3, and k is a constant.

From Figure 7 and using Eq. [1] the average values of kr for slags containing 2 and 3 mole pct Fe_2O_3 can be calculated. The calculated values of kr are listed in Table II.

Combining Eqs. [4] and [5] the specific rate constant, kr, can be written as

$$kr = \frac{RT}{2|Z_2|F^2} \int_{3.12 \times 10^{-12}}^{1} K_1 n_3 d \ln P_{O_2} \quad [6]$$

where $K_1 = ke\mu_3$ and is a constant.

Applying the values of kr from Table II in Eq. [6] we can calculate the constant K_1 for 2 mole pct and 3 mole pct Fe_2O_3 in the slag. As expected, the constant K_1 was nearly the same for 2 and 3 mole pct Fe_2O_3 in the slag. Therefore for the subsequent calculations the average value of K_1 is chosen (0.024). The overall slag conductivity when Fe_2O_3 is present can be expressed as

$$\sigma_\Sigma = \sigma_{ionic} + \sigma_{electronic} \quad [7]$$

where σ_{ionic} is the partial ionic conductivity and $\sigma_{electronic}$ is the partial electronic conductivity; both expressed as mho/cm.

On the basis of our earlier assumption that minute additions of Fe_2O_3 do not change the electronic mobility, we can write

$$\sigma_{electronic} = K_1 n_3 \quad [8]$$

and therefore

$$\sigma_\Sigma = \sigma_{ionic} + K_1 n_3 \quad [9]$$

Since the electronic conductivity is small, for all practical purposes σ_{ionic} in Eq. [9] is the overall slag conductivity with no Fe_2O_3.

Thus, we can use Eq. [9] to predict the slag conductivity with small additions of Fe_2O_3. On applying Eq. [9] to our analysis at 1173 K we should theoretically have an increase in the conductivity by 0.005 $(\Omega cm)^{-1}$ and 0.0007 $(\Omega cm)^{-1}$ for 2 mole pct and 3 mole pct Fe_2O_3 additions, respectively, to the slag. These increases, as we see, are rather small. From Figure 7 we can see that when we add 2 and 3 mole pct Fe_2O_3 to the slag, there is a small increase in the conductivity which is comparable with the predicted increases.

Therefore, in principle the above analysis tells us that minute additions of Fe_2O_3 will not drastically enhance the slag conductivity. This fact has also been noted by earlier workers.[7,8] However, as the rate controlling step is electronic transport (transport of holes), a very slight variation in the concentration of holes '(+)' can result in having a large variation in the oxidation rate of the liquid lead underneath the slag

C. Effect of Insertion of Ir Wire

It was observed that when ten Ir wires were used to short circuit the gas/slag and slag/metal interfaces, the oxidation rate increased by more than ten times as compared to when no Ir wire was used. The oxidation rate with and without the presence of Ir wires at $P_{O_2} = 1$ atm for a slag height of

Table II. Numerical Values for Oxidation Rate as a Function of Slag Depth for Slags Containing Fe_2O_3. Temperature 1173 K

Slag Number	Slag Depth	Additive	Oxidation Rate	Kr	P_{O_2}
1	2.5 mm	2 mole pct Fe_2O_3	6.12×10^{-8} equiv/cm^2-s	1.53×10^{-8} equiv/cm-s	1 atm
2	2.5 mm	– do –	6.04×10^{-8} equiv/cm^2-s	1.51×10^{-8} equiv/cm-s	– do –
3	3.7 mm	– do –	4.10×10^{-8} equiv/cm^2-s	1.52×10^{-8} equiv/cm-s	– do –
4	6.0 mm	– do –	2.5×10^{-8} equiv/cm^2-s	1.50×10^{-8} equiv/cm-s	– do –
5	2.5 mm	3 mole pct Fe_2O_3	7.28×10^{-8} equiv/cm^2-s	1.50×10^{-8} equiv/cm-s	– do –
6	3.7 mm	– do –	4.90×10^{-8} equiv/cm^2-s	1.81×10^{-9} equiv/cm-s	– do –
7	6.0 mm	– do –	3.06×10^{-8} equiv/cm^2-s	1.84×10^{-8} equiv/cm-s	– do –

Average value of Kr for slags with 2 mole pct $Fe_2O_3 = 1.52 \times 10^{-8}$ equiv/cm-s
Average value of Kr for slags with 3 mole pct $Fe_2O_3 = 1.82 \times 10^{-8}$ equiv/cm-s
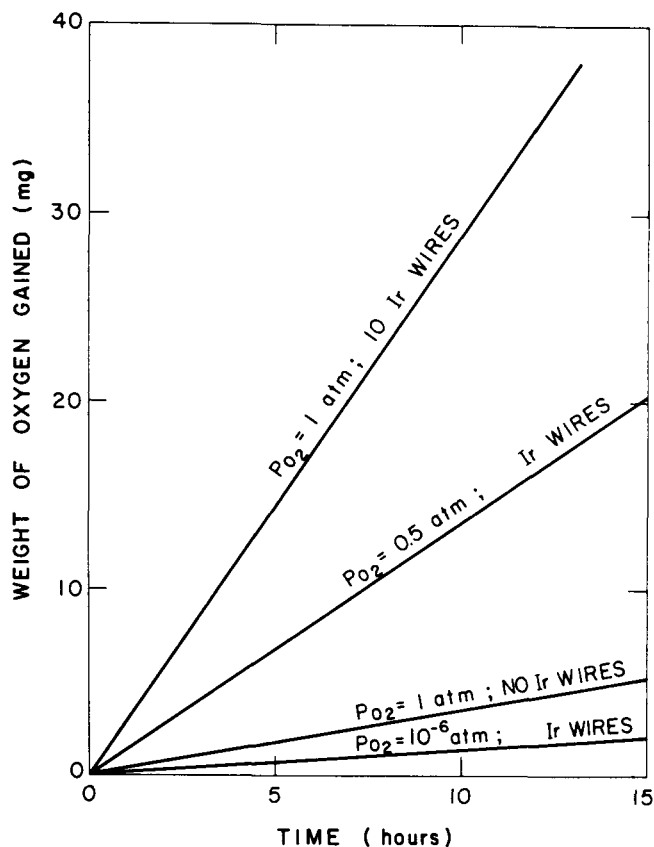
Fig 10—Oxidation plots of liquid lead covered by slag (55 mole pct PbO and 45 mole pct SiO_2) at $P_{O_2} = 1$ atm, indicating the effect of short circuiting the slag/gas and slag/metal interfaces with Ir wires

2.5 mm is shown in Figure 10. From these plots we can conclude that when the barrier to electronic transport is removed by inserting conducting Ir wires, the oxidation of liquid lead occurs with relative ease.

IV. SUMMARY

It was proposed that the oxidation of liquid lead covered by liquid $PbO-SiO_2$ melt occurs with the transport of elec-tron holes and lead ions in maintaining electrical neutrality. The electronic transport number (t_3) was determined to be of the order of 10^{-3}. Furthermore, using Wagner's oxidation theory it was established that the oxidation of liquid lead under our experimental conditions was diffusion controlled.

Addition of small amounts of Fe_2O_3 to the slag moderately increased the oxidation rate of the lead underneath the slag. However, when Ir wires were used to short circuit the slag/gas and slag/lead interfaces, the oxidation rate of the lead increased drastically, indicating that the electronic transport is the rate controlling step for oxidation.

Additions of Fe_2O_3 to the slag increased its conductivity very slightly. However, it was seen that with Fe_2O_3 the slag behaved as an n-type material at P_{O_2} less than 10^{-3} atm and as a p-type material at P_{O_2} greater than 10^{-3} atm.

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