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PbO SOLUBILITY IN LEAD BLAST-FURNACE SLAGS

by

Mark Edward Schlesinger

A Thesis Submitted to the Faculty of the

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1985

STATEMENT BY AUTHOR

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D. C. LYNCH
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Dec. 2, 1985
Date

PREFACE

The thermodynamic study of metallurgical slags has long been motivated by one primary consideration, improvement in performance of those smelting and refining operations with which these slags are associated. A particular point of concern has been limiting metal content of these slags; this concern has been extended to the study of viscosities and of component activities. However, the philosophical background of slag research has remained constant.

Recent years have seen a new reason develop for concern over slag chemistry, namely its characteristics as a waste material. This concern particularly applies to slags bearing toxic elements, such as lead, cadmium, arsenic, etc. Several studies have fueled controversy over the degree of "hazard" associated with slag dumping and over the methods of testing used. A particular point of contention is the Environmental Protection Agency's use of a test procedure developed for municipal waste dumps, which is claimed by others to be inappropriate for use with slags (Robbins, Bundy and Stanga, 1983). Other issues include the effects of rain acidity, slag structure and surface area, and dumping method.

One factor which may have a significant impact on test results is slag composition and morphology; unfortunately, these have rarely been consistent even within the various studies mentioned above. Since the molecular structure of a slag is very much related to its chemical composition, (Masson, 1972) changes in that composition could make a significant difference in its

response to hazard level testing. These effects have yet to be thoroughly examined, as emphasis has instead been placed on research with actual slags.

Part of the difficulty in initiating controlled-composition studies is a lack of basic phase-diagram data for slag systems. Most slags contain four or more major components, but research on even ternary systems is largely incomplete. This is especially so in systems associated with non-ferrous metallurgy, the source of many potentially toxic elements. For these systems, environmental concerns have thus joined metallurgical needs as a justification for thermodynamic research.

One of these slag systems is that of the lead blast furnace. Its composition varies with the ore being processed, but usually includes silica, alumina, calcia, and iron and zinc oxides, along with measurable percentages of lead and lead oxide. The lead content is found in two forms, dissolved PbO and small lead "droplets" which failed to settle out of the slag before its being tapped. Slag Pb content varies between smelters, and has been related to several factors, most notably the ratios of other slag components. Furthermore, the lead distribution between various slag phases and relative Pb/PbO ratios also vary and have been related to the melt composition. This varying morphology could very well be a source of variation in the results of toxicity tests for even those slags with comparable overall levels of lead. However, testing this possibility has not been feasible, due to a lack of thermodynamic data for accurate prediction of slag Pb or PbO content at a given temperature.

The research described herein represents an attempt to improve upon this unpredictability. As a compromise between practicality and the com-

plexity of real slags, this research deals with a four-component system: SiO_2, CaO, $FeO_{1.0-1.5}$, and PbO in equilibrium with molten lead or a lead alloy. By varying the slag composition, it was hoped to effect changes in the PbO/metal equilibrium, and ultimately to derive that equilibrium as a function of the composition at a given temperature. This in turn would allow the "design" of slags for controlled toxicity studies to be conducted in the future. The potential reduction of Pb loss in smelter slags was also a possible result, one which would again demonstrate the new dualism in the justification of slag system thermodynamic research.

I would like to express my deepest appreciation to my thesis director, chief advisor, svengali, etc., Prof. D. C. Lynch, for making this (such as it is) all possible. I would also like to thank the other graduate students in the Department of Materials Science and Engineering (neé Metallurgy), for their forbearance and understanding while I completed this work. Last (but not least) I would like to express my appreciation of the Mining and Minerals Resource Research Institute for their financial support during this time.

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ABSTRACT

The solubility of lead oxide in slags equilibrated in contact with molten lead and lead alloys has been determined at 1200^{o}C. At low lead levels, this solubility is primarily related to the system's oxygen partial pressure; the latter is itself expressable as a function of the slag chemistry, particularly the relative levels of basic and acidic oxides. Two models have been employed in evaluating this relationship. The first, empirically determined from a similar study, is related to the thermodynamic equilibrium between lead and slag phases; the second is derived from considerations of the structure of oxide/silicate melts, and is applicable to more complex systems. The degree of agreement between the results obtained from use of these models improves when questionable assumptions about the behavior of less basic oxides in the slag structure are discarded.

CHAPTER 1

INTRODUCTION

Without regard to the particular metal being smelted, a blast-furnace slag may be generalized as "a silicate combined with a basic oxide" designed for separating the gangue materials of an ore from the molten reduced metal (Dennis, 1965, p. 176). Within this definition, there is considerable variation between systems, and a study of that of the lead smelter requires special consideration of its components.

In the earliest blast furnaces, lead smelting slags were often a mixture of only two major components, silica and iron oxide. Later smelters began to add to this significant levels of calcia, either as limestone or burnt lime (Collins, 1899, p. 112). The CaO reduced the slag viscosity, which resulted in lower lead and silver losses in the slag; it apparently was also cheaper than the iron oxide it replaced. This system is largely the one still used today.

The reader will notice that to this point the rather generic term "iron oxide" has been used, without regard to oxidation state. That state varies of course with the blast furnace's oxygen partial pressure, but in general is mostly ferrous (divalent). Too much ferric (trivalent) oxide increases the slag's viscosity, which in turn makes slag-metal separation difficult and increases bullion losses (Matyas, 1975; Matyas and Street, 1977). In fact, most analyses of commercial slags express iron content as entirely FeO. For convenience, this discussion will do the same.

These three components - SiO_2, CaO and FeO - are the main constituents of lead blast furnace slag, comprising sixty to eighty percent of its total weight in most analyses (Cotterill and Cigan, eds., 1970, pp. 346, 416, 599, 643, 696, 742, 766, 786,800, 856 - authors of the specific papers are named in the List of References). The remaining material is also important, however, and deserves some mention. It can be divided into two categories: that introduced to the blast furnace as a flux (like the CaO and FeO), and that brought in with the roasted concentrate.

Calcia and iron oxide are known as 'basic' oxides, and are sometimes partially replaced by others in this group. Manganous oxide (MnO) has long been noted as a means of reducing a slag's melting point, especially in low-silica compositions (Collins, 1899, p.128; Rosenqvist, 1974, p. 328). Less noted for this is the addition of barium oxide (Hofman, 1918, p. 324). Another means of reducing fusion temperatures has been the use of fluorspar (CaF_2), again most often in low-silica slags. These 'off-beat' fluxes tend to be costly, however, and are held to less than five percent of the slag weight when used.

The importance of keeping slag silica contents low is that compositions with a high ratio of basic oxides to SiO_2 absorb more sulfur from the blast furnace reduction process (Rosenqvist, 1974, p. 332-33). This can range up to 2.5% S. Most lead ores also contain a good deal of zinc, which reports to the slag as ZnO. Analyses of more than twenty percent ZnO have been noted, and this too recommends low SiO_2 levels (Collins, 1899, p. 116). Other ore gangue components include magnesia (under three percent in most slags), and alumina (as much as six percent), neither of which is particularly useful in

slag "design". Finally, the silica content of lead blast furnace slag is generally brought in with the concentrate as well.

There is one final constituent of the concoction that merits special attention - lead. Most smelters work hard to minimize its presence, but it can still reach to over three percent. The blast-furnace partial pressure of oxygen is an especially important factor in this, as its increase 1) encourages PbO foruation, and 2) increases ferric oxide content, with the deleterious results described above. As shall be seen, most of the existing literature on lead-smelting slag thermodynamics has been done to find ways of reducing lead contents.

The form in which lead is found in slag is not necessarily constant. Much of it is present as small droplets of the metal, possibly 85% of the total slag Pb present (Matyas and Street, 1977). A PbO content of .5-1.5% is indicated by other work (Matyas, 1975). Still other investigators have found that metallic lead is also soluble in slag, though only the about .1% (Richardson and Meyer, 1956).

As a final note to this discussion of lead-smelter slag chemistry, it should be noted that the compositions mentioned are those of slags dealt with by disposal. The newer direct-smelting processes for lead production produce a different type of slag, with 15-50% total Pb - mostly as the oxide (Matyas and Mackey, 1976). This is then itself smelted in a second step, which produces a slag similar to that of the roasted-concentrate blast furnaces.

As earlier noted, a major factor in the amount of lead in solution in a slag (preponderantly PbO) is the partial pressure of oxygen in the system;

since this also largely controls the ratio of ferric to ferrous iron content, it is not surprising that researchers have attempted to correlate the two. Notable in this vein is the study of Sugimoto et al. (1977), and more so that of Taskinen et al. (1984). What Taskinen et al. have shown is that the oxidation state of Fe is not by itself a way of accurately predicting slag PbO content. To it must be added the effects of other slag components, most notably the CaO and SiO_2 contents, which can themselves be expressed as a ratio. The reason for this, as demonstrated in several earlier papers (Kyvatkovskii et al., 1981; Lenz and Lee, 1981; Meyer et al., 1966; Ouchi and Kato, 1983; Sugimoto and Kozuka, 1978; Taskinen et al., 1982), is that increased CaO/SiO_2 ratios increase the activity coefficient of PbO in the slag, while at the same time decreasing the solubility. Taskinen et al. (1984) also have shown that higher total ratios of iron to silica also reduce PbO solubility. Clearly oxygen partial pressure is not the only factor in determining slag lead contents.

The reason for this lies in the molecular nature of molten silicate slags. To quote a leading researcher of the topic (Masson, 1972), "liquid silicates are polyionic melts which contain, in addition to cations and free oxygen ions O^{2-}, an array of silicate ions of varying size and complexity in a state of dynamic chemical equilibrium." Along with this, it has been recognized that increasing content of the basic metal ions that help make up the silicate structure decreases the size of the polysilicate molecules, thus making available more "spaces" within the structure to fit impurities (such as PbO). Some basic oxides are more capable of accomplishing this than others, CaO being among the most effective. Other such oxides (MgO, ZnO,

BaO) have also been shown to increase the activity of PbO in slags (Ouchi and Kato, 1983; Sugimoto and Kozuka, 1978). FeO also counts to a lesser degree as a basic oxide, with a similar effect on the slag structure (Sugimoto et al., 1977).

The large number of components in the typical lead blast furnace slag has made it difficult to derive a mathematical means of predicting PbO solubilities. Most of the studies cited above were limited in scope to three components (including SiO_2) or less; however, the recent work of Taskinen et al. (1984) employed a five-component system including Fe^{2+}, Fe^{3+}, Si, Ca and Pb oxides, and Vaskevich et al. (1983) have reported experiments on a similar system, without CaO but including ZnO and Al_2O_3. These studies, particularly that of Taskinen et al. (1984), are certainly a major improvement in our comprehension of how slag chemistry parameters affect lead oxide solubilities. However, they still retain some deficiencies that recommended further work. Firstly, most of Taskinen et al.'s data was derived from slags with PbO contents of 20 to 50 percent. While this accurately depicts compositions in the direct-smelting type of slag (Fontainas and Maes, 1979; Schwartz et al., 1979), it is perhaps less useful as a model for the less-than-10% PbO contents of the blast furnace. The temperature choice of 1300°C is also higher than normally used (Lenz and Lee, 1984). Lastly, the ferric/total iron ratios used by Taskinen et al. are higher than those normally encountered in oxide smelting. For those reasons, it was decided to perform a similar study at 1200°C, with an aim toward producing an accurate model for lead oxide solubilities at low PbO ranges.

CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 A Review of Experimental Methods

As earlier suggested, the key to successful slag thermodynamic research, especially in a relatively complex system such as the SiO_2-CaO-FeO_x-PbO mixture, is the ability to control as many degrees of freedom as possible. As the Gibbs phase rule points out, in a five-component system (Fe-Ca-Pb-Si-O) with three phases (liquid metal and slag, and vapor above the melt), the degrees of freedom available are equal to 5 - 3 + 2 = 4. Setting the temperature removes one of these; further reduction requires chemical control of the material to be equilibrated.

One way of chemically eliminating a degree of freedom from a molten slag system is to artificially set the partial pressure of oxygen in the vapor phase. This can be done by passing a known mixture of CO and CO_2 over the molten slag, which will then respond by changing its equilibrium state to match that required by the gas mixture. This method has found use in several of the studies mentioned above (Matyas, 1975; Saito, 1957; Kyvatkovskii et al., 1981; Zaitzev et al., 1972; Vanyukov et al., 1966). It is, however, limited in two aspects: it requires the use of a large volume of gas mixture in relation to the amount of slag, and is a source of restriction of the species in the condensed phase, particularly volatile ones. As shall be seen, the latter is a more serious restriction than is apparent at this point.

Most lead blast-furnace slags are created under a partial oxygen pressure on the order of 10^{-10} atm. In translation to experimental practice, this means that even if a CO/CO_2 mixture is not found usable, a means does have to be found for limiting oxygen exposure to the equilibrating slag mixture. One common method is the use of an extensive purge with argon (Taskinen et al., 1982; Taskinen et al., 1984; Sugimoto and Kozuka, 1978) or nitrogen (Richardson and Pillay, 1962). Of course, the use of these gases yields the same concerns about volatile species in the slag melt as previously mentioned. A third means of limiting O_2 availability is the use of a sealed crucible or ampule (Meyer et al., 1966; Meyer and Richardson, 1957). As with the argon and nitrogen methods, use of this allows the equilibrating slag to set its own partial pressure. The use of this "closed" system removes the concerns associated with open-system methods, but presents problems of its own, most notably those of materials and sealing technology. An experiment to be conducted at 1200^{o}-1300^{o}C for several hours is not as easily constructed as those designed for lower temperatures.

Other degrees of freedom may be removed in the makeup of the slag itself. Several investigators have shown the value of setting the ratios of various slag components, most notably CaO/SiO_2 and Fe/SiO_2 or FeO/SiO_2. This allows the variance of other components and the expression of the resultant equilibria as a function of the varied parameter. Lastly, it should be remembered that lead smelter slags are made in contact with molten lead, approaching equilibrium with that phase. Setting the activity of lead by equilibrating laboratory slag melts with pure lead or a lead alloy of some sort eliminates another degree of freedom. Of course, there is a limit on the

amount of lead that can be put in a laboratory-scale system, and pure Pb has a considerable vapor pressure at 1200°-1300°C. This is the main drawback against the use of gas mixtures in slag chemistry experiments, as there is no way of assuring that any Pb would be left in a crucible after the time needed to equilibrate an open-system slag.

It will be noted that the crucible itself has been largely ignored in this discussion. Actually, its inclusion can make a difference, depending on what material it is constructed of. For example, the use of a silica crucible would increase the number of phases in the system by one, but would offer no increase in the number of components; this would mean the removal of one degree of freedom. However, it would also mean limiting possible slag compositions to those saturated with SiO_2, an unrealistic condition. Alumina is also a common crucible material, and being a new component would not reduce the degrees of freedom in the system. The drawback in its use is that the slag under consideration for this study already had one more constituent than most similar experimental programs; Al_2O_3 would only have confused the issue.

Another choice of crucible material is graphite, which is certainly insoluble in slag. Its drawback is that its use would automatically set the O_2 partial pressure in much the same way as the CO/CO_2 mixture, and at much lower levels - again, an unrealistic condition. Iron crucibles are ruled out for much the same reason, as they effectively set the ratio of ferrous to ferric iron in the slag. In a more expensive vein, platinum has none of the drawbacks mentioned above, but it suffers from being soluble in molten lead at 1200°C. There is little point in using a crucible material that literally

melts in the furnace (not in your hand).

A more satisfactory choice would be a crucible material that could be effectively excluded from the system, and thus would not affect the number or limits on its degrees of freedom. F. D. Richardson at the British Institution of Mining and Metallurgy found such a material in iridium metal (Meyer and Richardson, 1957; Richardson and Pillay, 1962; Meyer et al., 1966). Ir is noble enough to be unoxidized under the conditions of slag equilibrium, and is insoluble in bwth slag and molten lead. It is probably the best choice for crucible material, with the exception of one matter - cost. Iridium crucibles could "break the bank" of even the most affluent project, and thus are rarely used.

The choice finally used for this investigation was that employed by the group headed by A. I. Taskinen at the University of Helsinki's Institute of Process Metallurgy (Taskinen et al., 1982; Taskinen et al., 1984). Calcia-stabilized zirconia is slightly soluble in molten slags, but work exists showing that its effect on the activity of PbO in a lead silicate melt is minimal (Kuxmann and Fischer, 1974). Since the CaO content in crucibles of this material generally ranges between three and five percent, the concern with constituent saturation that rules out silica crucibles can also be discerned. Lastly, ZrO_2 crucibles are considerably less costly than iridium; this proved the telling point in the decision to employ that material. (ZrO_2 crucible are not, however, sold by just anyone. Two sources are Alfa Products of Danvers, MA, and Zircoa Products of Corning, NY.)

As mentioned earlier, a reason for pursuing this study was the production of slags with controllable - and appropriately low - lead contents, and

one way of doing so thought worth a try was reducing the activity of Pb in contact with the molten oxide mix. Most of the slags in the above studies were equilibrated in contact with pure molten Pb, thus setting the activity of lead at unity. Changing the activity of lead would not change the O_2 partial pressure, nor would it affect the activity coefficient of PbO in the slag; a_{Pb} would (as a result) be directly proportional to the lead oxide solubility. For example, creating a metal phase with an a_{Pb} of .5 would halve the PbO presence in the slag. This seemed like a good idea, so a metal suitable for creating such an a_{Pb}-reducing alloy was sought.

Such a metal had to fulfill several requirements. First of these was insolubility in slag; a soluble metal would add one more degree of freedom to the system. Second was the existence of a broad range of liquid solutions at 1200°C, with a complete range being even better. Third, this metal had to be noble enough to avoid oxidation in the sealed system; fourth, it had to be inexpensive enough to match a reasonable budget. Finally, the system of this metal and lead had to have been studied enough to allow for reasonable prediction of Pb activity versus composition in it at 1200°C. Ultimately, the ansser to these requirements was silver; the activity data compiled by Hollitt et al. (1984) was chosen as the most accurate of several available thermodynamic investigation reports.

2.2 A Little Research History

Figure 1 depicts the original regime used in this investigation. Although too small to be shown in the figure, a thimble-size ZrO_2 crucible filled with a mixture of "slag-forming" oxides and lead metal was suspended

1. Vertical tube resistance furnace; 24 in. length, 2 in. I. D.
2. Alumina furnace tube; 36 in. length, 1 in. I. D.
3. Type R thermocouple connection and lead wire.
4. Alumina thermocouple protection tube.
5. Gas inlet tubing (1/4 in. Tygon).
6. Alumina gas purge tube.
7. Gas outlet tubing (1/4 in. Tygon).
8. Cooling water inlet and outlet tubing (1/8 in. Tygon).
9. Copper cooling water coil (1/8 in. tubing), and aluminum foil sleeve.
10. Fiberfrax ceramic wool plug between furnace tube and furnace wall.

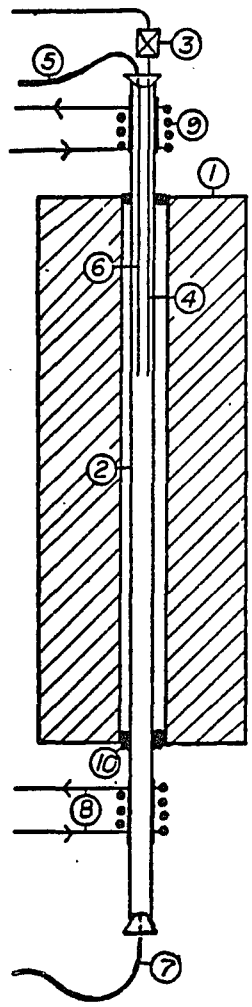

Fig. 1. Cross-section of resistance furnace for slag equilibration experiments.

from the top stopper with the use of a platinum-wire "cage," hanging at a level just below that of the thermocouple protection and gas introduction tubes. It will be noted that an open system was the first choice of procedure, despite the risk of Pb loss from the crucible. The use of molten Pb in equilibria with the slag melt and the use of a CO/CO_2 gas mixture set two degrees of freedom; the other two were set by the choice of a Fe/SiO_2 ratio of 1.17, and (initially) by the selection of CaO/SiO_2 ratios of .47, .57, .67 .75 and .82, for better comparison with the work of Taskinen et al. (1984). Table 1 shows the choice of reagents for the slag mixture; as those familiar with the Fe-O phase diagram will recall, stoichiometric ferrous oxide does not actually exist. It can however be approximated by a mixture of Fe metal and wustite ($FeO_{.95}$). Previous investigators have also approximated FeO with a mixture of metal and Fe_2O_3; it was felt that in this case the use of a commercially-manufactured wustite "FeO" would make equilibration of the system more easily accomplished, thus justifying its higher cost.

The choice of platinum wire to hold the crucible up inside the furnace was in retrospect not the best; the later-adopted use of firebrick "sticks" would have been more advisable. However, the Pt wire did prove useful in demonstrating to the investigator just how unworkable the open-system setup was. As previously intimated, lead and platinum form a series of liquid alloy compositions at 1200°C, and experiments with the regime shown in Fig. 1 failed without exception when this alloying between Pb vapor and the wire caused the latter to break, thus dropping the crucible. This led to the additional realization that the loss of Pb in this particular system would be too great a problem to adequately solve. In summary, it became obvious that

Table 1

List of Reagents Used for Slag-Metal Equilibration

Reagent	Supplier	Purity
Calcium Oxide	Alfa Products	99.95%
Ferric Oxide	Alfa Products	99.9%
"Ferrous Oxide"	Alfa Products	99.9%
Lead (metal)	ASARCO	99.9%
Lead Oxide	ASARCO	99.8%
Silicon Dioxide	Alfa Products	99.5%
Silver (metal)	Alfa Products	99.999%

Note: With the exception of ferrous oxide, these reagents are widely available from suppliers other than those listed. "Shopping around" is recommended.

a closed system would be required.

The choice of 1200°C as an equilibration temperature has been mentioned above. As also mentioned, this seems a somewhat more realistic temperature than the 1300°C used by Taskinen et al. (1984). In addition, it was also the maximum temperature consistent with continued use of the Kanthal windings in our furnace. In fact, 1150°C was the original choice of temperature, and was abandoned only because the slag mixtures failed to fuse at this level. Figure 2, a copy of the $FeO-SiO_2-CaO$ pseudoternary phase diagram, and Fig. 3, the $Fe_2O_3-SiO_2-CaO$ pseudoternary, show that only a few compositions have melting points below 1150°C, and that increasing ferric iron

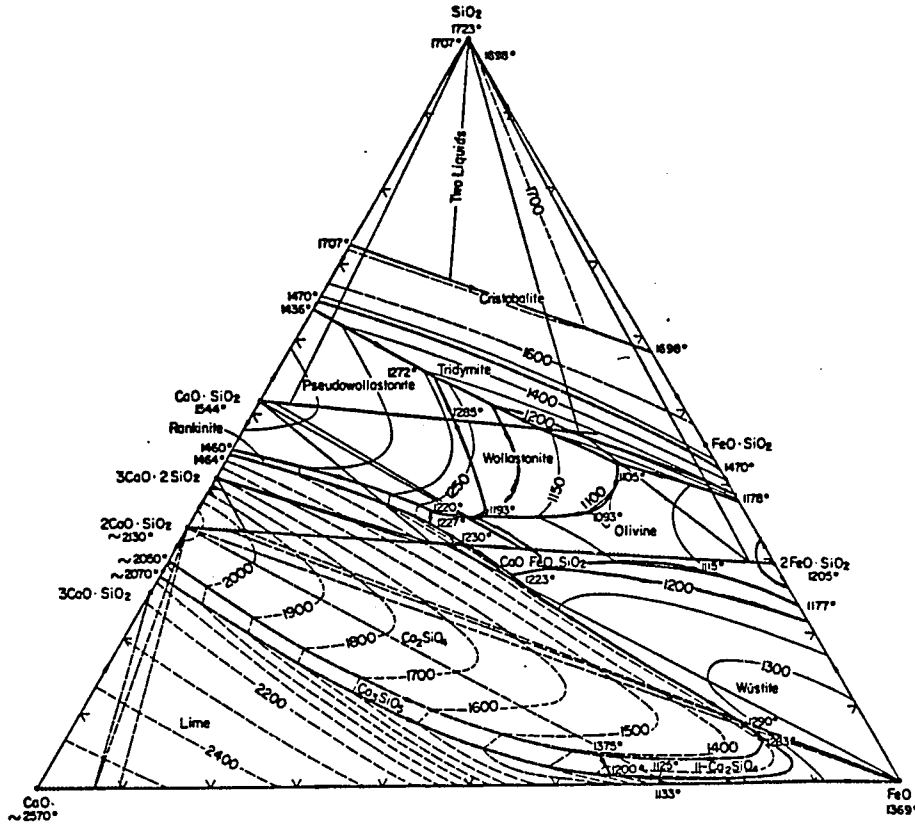

Fig. 2. The $FeO-SiO_2-CaO$ pseudoternary liquidus surface. From Levin et al. (1964), p. 204.

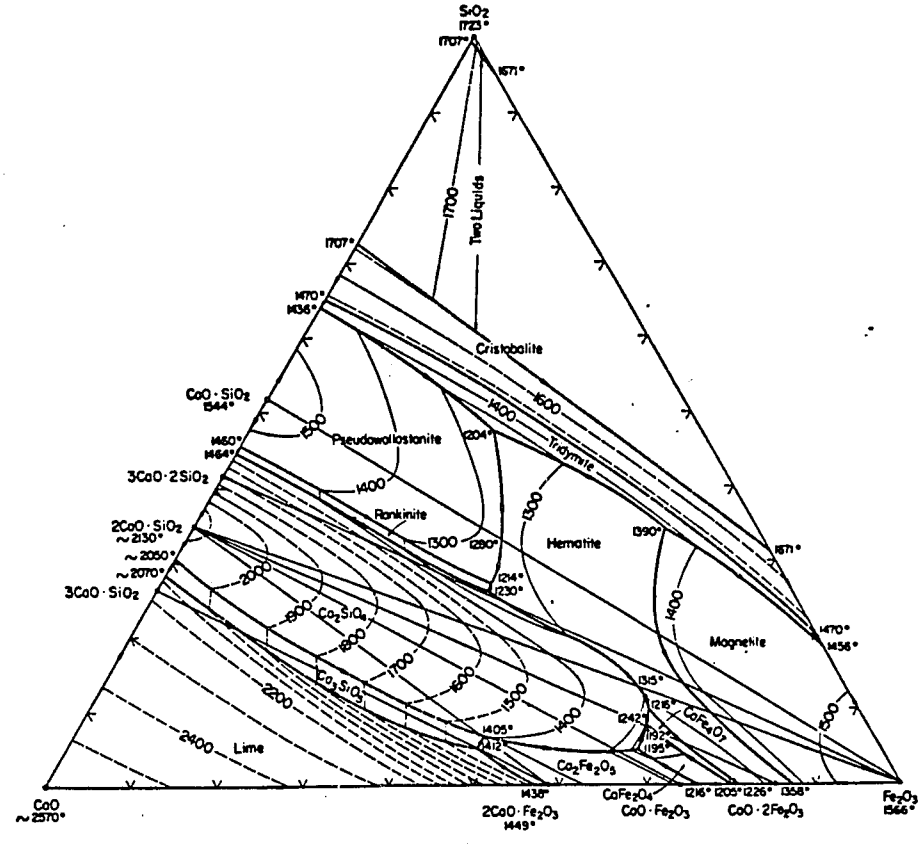

Fig. 3. The Fe_2O_3-SiO_2-CaO pseudoternary liquidus surface. From Levin et al. (1964), p. 228.

oxide content makes these liquidus temperatures even higher - as do increasing CaO/SiO_2 ratios. As a result, it was decided that in addition to the furnace temperature increase and choice of a closed system, that the range of calcia/silica ratios would also be changed from those used by Taskinen et al. (1984) to .40, .47 and .57. Later on, it was discovered that higher-ratio slags would also fuse at 1200°C, leading to the equilibration of a small series of melts with $CaO/SiO_2 = .80$, along with $CaO/SiO_2 = .10$.

Earlier discussion of the closed-system method of slag equilibration noted that one of its main drawbacks was the technical difficulty in sealing ampules. A main facet of the problem was that the ampule had to be sealed under vacuum, in order to limit the amount of oxygen available to the system. Too much oxygen would 1) create an equilibrium inappropriate to the system, and 2) increase the risk of pressure buildup and ampule rupture. Another problem with the sealed ampule is the adsorption of water vapor by the reagent chemicals sitting in the crucible. In an open system, this water would be purged from the system by the covering gas as the temperature rose to the point where it desorbed from these chemicals. The use of a closed system required the development of a method for removing this water from the mixture in the crucible before its sealing; otherwise, it too would become a source of excess oxygen presence in the equilibrating system.

Figure 4 is a schematic of the apparatus ultimately derived to solve these problems. The outer "skin" of the ampule was a 16 x 14 (16 mm. O. D., 14 mm. I. D.) length of fused silica tubing. Two five-inch sealed 10 x 8 silica tubing sections formed a support for this outer skin as it collapsed under the heat of a hydrogen-oxygen flame and the stress of a rotary-pump

1. Outer ampule cover (fused quartz tubing) - 16 mm. O. D. x 14 mm. I. D., 15 in. length.

2. Inner support tube (fused quartz; two req'd.) - 10 x 8, 5 in.

3. Fiberfrax ceramic blanket (small hunk).

4. Anhydrous calcium sulfate (Drierite).

5. Crucible hood (fused quartz) - 13 x 11, app. 1 in.

6. Crucible (CaO-stabilized ZrO_2) - app. 10 x 8, .5 in.

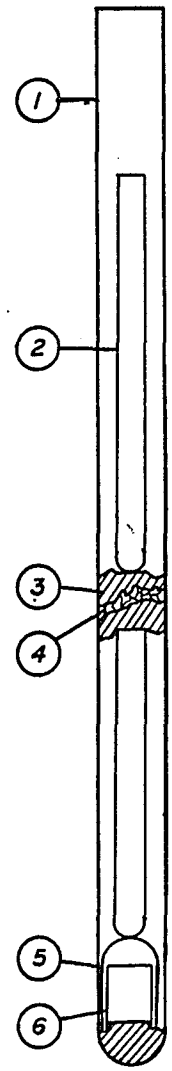

Fig. 4. Ampule-sealing apparatus.

vacuum (20-mμ pressure). Attempts at this sealing without the support tubing resulted in considerable breakage of the 16 x 14 ampule. The material between the support tubes was a "sandwich" of sorts, more specifically several small pieces of anhydrous calcium sulfate (Drierite) between two wads of Fiberfrax ceramic wool. This was the solution, as shall be seen, to the adsorbed water concern. The crucible itself was covered by a "hood" of 13 x 11 fused silica tubing, to prevent contamination of the mixture inside by falling Fiberfrax or Drierite. The whole assembly was initially sealed at the bottom, and the very first thing put into it was a small wad of Fiberfrax; this protected the bottom from the shock of other things being pushed into it.

Once the 16 x 14 tube had been collapsed onto the 10 x 8 tube along a width of one to two inches, it became the equivalent of a 12 x 8 tube, easily sealed without undue fear of breakage. This was done twice in the ampule sealing process, the first time above the Drierite to isolate the system and ensure that the $CaSO_4$ could absorb only water desorbed from the mixture in the crucible. Placement of the bottom of the isolated ampule into a small tube furnace heated to 600°C ensured desorption of the H_2O, without heating the Drierite above the temperature at which its function could not be fulfilled. A 30-minute stay in the tube furnace was enough to accomplish this transfer of water, and at this point a second sealing operation between the Drierite and the crucible completed the manufacture of a closed system with a minimum of available oxygen.

One unresolved drawback of this system that deserves discussion is the size limitation imposed on the system by the furnace diameter (one inch) and the glassware required. This in turn required the use of a very small ZrO_2

crucible, and meant that sample sizes were a compromise between the amount needed to get enough material for analysis and the limitation of available volume. Seven tenths of a gram of slag mixture usually fit, but only at the risk of spillage if care was not used.

The time needed to equilibrate slag mixtures varies a good deal in the literature; this is related to disparities in experimental methods, sample sizes, laboratory equipment, etc. Due to the low-weight slag mixtures, it was found that only eight to ten hours were needed to ensure complete equilibrium. (However, other facets of the research were affected by equilibration time, as shall be seen.) As earlier mentioned, a column of pieces of firebrick supported at the bottom of the alumina furnace tube was selected as an improved method of holding the ampule up in the furnace; the bricks tended to crumble under the heat, but were easily replaced. Since an ampule under vacuum may not be as good a conductor of heat as an unadorned crucible, there was concern that it might not be possible to quench the molten slag at a rate fast enough the prevent phase separation; had this been so, it would have been impossible to properly examine the molten system equilibria. Fortunately, water-quenching of the ampule proved to yield a cooling rate adequate enough to 'glassify' the freezing slag mixture. Following this, the crucible inside was recovered by simply breaking open the ampule with a hammer.

Appendix A shows the simple computer program used to calculate initial charge weights. For lack of a better choice, it was assumed 1) that our results would match those of Taskinen et al. (1984), and 2) that the oxygen remaining in the sealed ampule was minimal enough compared to the mass of

slag mixture to effect very little change on the equilibrium. The choice of Fe/SiO_2 ratio (1.17) was also a function of our desire to obtain data comparable with that of Taskinen et al., although it is somewhat high in relation to "real" slag ratios. Initial "aimed-for" PbO solubilities of 15, 20 and 25 percent were chosen, higher than the levels of the controllable-composition slags ultimately sought; a similar set of experiments was run with a lead-silver alloy with an initial Pb activity of .25, to hopefully produce more usable data. The result in each set was thus two experiments at each of three calcia/silica ratios and three projected PbO percentages, a total of 18 samples in each half of the experimental program. Later on, a "supplementary" set of seven experiments was done with calcia/silica ratios of .10 (three) and .80 (four).

CHAPTER 3

ANALYTICAL METHODS

As earlier noted, the slags manufactured in this program contained five "components", namely Fe, Si, Ca, Pb and O. In addition, the iron in these slags existed in two oxidation states, ferrous (Fe^{2+}) and ferric (Fe^{3+}), the ratios of which were of critical importance to the experimental results. Since the slag oxygen contents were related to the percentages of the other components, that meant that five analyses of every slag were needed to achieve a complete chemical description. A sixth analysis was also required from those slags equilibrated in contact with lead of less than unit activity; i. e., the final Pb-Ag alloy contents. Given the small amounts of slag available to this investigator for these analyses, the development of routines capable of yielding reproducible results from very small samples became a matter of great importance.

The most difficult challenge in analytical routine development was that of assessing the ferric/ferrous iron ratios. Most of the methods listed in the literature require 0.5-1.0 gm. of slag (Young, 1971, pp. 181-83); unfortunately, our experiments began with only 0.7 gm. of reagent mixture, and after separating the resultant quenched slag from the crucible and metal, recovering half of this amount for analysis was considered fortunate. Furthermore, it should be recalled that some of this material was needed for analysis of the Si, Ca and (most importantly) Pb contents. Therefore, a fer-

rous/ferric analytical method was needed which would allow for the use of samples on the order of 30 milligrams of slag. Previous experience in connection with similar research had fortunately uncovered such a method, thus saving considerable time and effort.

The ferric/ferrous analytical method adopted is a descendant of that employed by Marschman (1983), itself adapted from the works of Harvey et al. (1955) and of Fortune and Mellon (1938). This method relies on the broad, well-defined spectrophotometric absorbance peak of the 1,10-phenanthroline-iron(II) complex, and the ability of certain reagents, such as hydroxylamine hydrochloride and hydroquinone, to reduce Fe in solution to the ferrous state without causing interference in the absorbance reading of such a complex. The creation of two solutions from a digested slag sample, one so reduced, would yield the percentages of total and ferrous iron in the slag, the difference being the ferric iron content and the solution of a difficult analytical challenge.

Figure 5 illustrates the apparatus set up to perform such an analysis. The considerable amount of tubing required to build this apparatus is due to the requirement that slag digestion and dilution be performed under a pure nitrogen (or inert gas) atmosphere; otherwise, the heat of digestion would cause oxidation of much of the ferrous iron in the sample to ferric, ruining the results. Digestion was accomplished with the addition of reagent-grade 36% hydrochloric acid from the buret atop the digestion vessel. (A full list of reagents used in the various analytical routines can be seen as Table 2.) HCl was used because previous work (Harvey et al., 1955) had shown it to be the anion least likely to cause interference with the phenanthroline-iron(II)

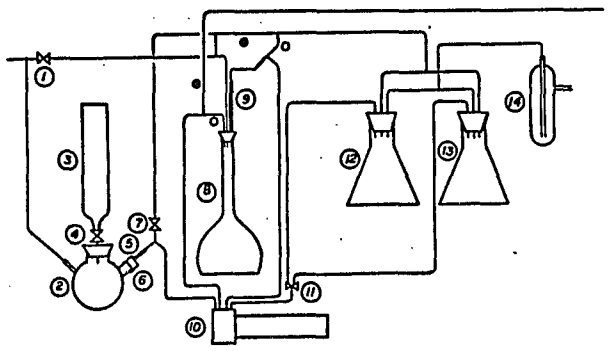

Fig. 5. Ferrous/ferric iron analytical setup.

1. Nitrogen control stopcock.
2. Digestion vessel (500 ml. round-bottom flask).
3. HCl and dilution buret (250 ml.).
4. Buret stopcock.
5. Diluted solution nozzle (2 ml. glass pipette).
6. Rubber septum (3/4 in. I. D.).
7. Diluted solution stopcock.
8. Diluted solution vessel (1000 ml. volumetric flask).
9. Solution distribution nozzle (8 mm. O. D. Pyrex tubing, 10 in. length).
10. Peristaltic pump (2-line capacity).
11. Solution distribution stopcock.
12. Ferrous iron flask (500 ml. Erlenmayer).
13. Total iron flask (500 ml. Erlenmayer).
14. Air seal (bubbler with dibutylphthalate in bottom).

Filled circles indicate locations of pinchcocks before distribution step; hollow circles indicate locations otherwise. Tubing between diluted solution vessel and peristaltic pump and between pump and solution distribution stopcock is 1/8 in. Tygon; elsewhere, 1/4 in. Tygon.

Table 2

List of Reagents for Analytical Routines

Reagent	Supplier	Purity
Boric Acid	Fisher Scientific	99+%
Ferrous Ammonium Sulfate	Mallinckrodt	99+%
Hydrochloric Acid	MCB Reagents	36%*
Hydrofluoric Acid	MCB Reagents	48%*
Hydroquinone	Aldrich Chemical	98.5%
Nitric Acid	J. T. Baker	70%*
1,10-Phenanthroline Monohydrate	Aldrich Chemical	99+%
4,2-Pyridylazo Resorcinol	GFS Chemicals	99+%

* - Nominal percentages only; actual purities may vary.

Note: These reagents are all available from several sources, and "shopping around" is recommended.

absorption peak (along with the fact that Marschman had used it without problems). One slight difficulty in the procedure was caused by the fact that the impact of HCl drops as they hit the bottom of the digestion vessel occasionally splattered small pieces of the powdered slag sample up the sides of the flask, away from acid contact. To make sure everything was eventually contacted, a small amount of water was later added to the solution (again through the buret), and the mixture briefly heated with a Bunsen burner to

ensure better mixing. Total slag digestion time was usually three to four hours; a complete version of this procedure is provided in Appendix B.

One facet of the ferric/ferrous analytical routine of some interest was the choice of the "center" wavelength for the complex absorption peak. The original investigation into this complex by Fortune and Mellon (1938) had shown a peak centered at 512 mμ, a figure agreed to by the work of Harvey et al. (1955). Marschman (1983) found that his complexes yielded the best readings at 520 mμ; the spectrometer used for this investigation, a Bausch & Lomb Spectronic 100, yielded a peak at just above 516 mμ. Rather than causing concern, this variance merely shows 1) that this peak, being so broad and well-defined, is particularly useful for this type of analytical work, and 2) that spectrometers are very much individual instruments, capable of being affected by such little things as ambient room temperature, phase of the moon, day of the week, etc. Another noteworthy item about this analytical routine was the "shelf life" of the 5.0 ppm iron standard against which measurements of the sample solutions were compared. Although it was felt that it might be necessary to make these up daily (from ferrous ammonium sulfate dissolved in ultrapure water and complexed with phenanthroline solution), it turned out that 500 ml. of a complexed standard solution was good for a month or more. It saved the investigator considerable work.

A final note about the ferric/ferrous analytical routine lies in the discovery that the choice of cuvet material is of more than some importance. Various anomalies in early analyses led to the finding that a mixed ferric/ferrous solution is slowly reduced by the polystyrene of disposable cuvets to an entirely ferrous solution, and that leaving a sample of solution in

such a cuvet for over two to three minutes can be hazardous to one's data. For this reason, dawdling on the taking of readings was expressly forbidden.

The other analyses required for chemical description of the experimental slags required a procedure for complete sample digestion, rather than the partial attack provided by the HCl used in the ferrous/ferric routine. This is not a simple matter, as the acids which might easily attack some of the slag components (HNO_3 easily dissolves iron, lead and calcium oxides, for example) may actually stabilize the solid state of others (such as silica). In addition, a "wild card" was added in the form of zirconia in the slag; the ZrO_2 presence meant that it was not possible to dissolve everything but the SiO_2 and assume that component to be the difference. The relatively high lead contents of these slags also were a potential source of difficulty, since PbO is only slightly soluble in HCl, insoluble in HF, and highly soluble only in the unusable HNO_3. As earlier intimated, most slags contain a good deal less Pb content than these, and this meant that much previous analytical experience was of limited applicability. As it developed, as much developmental work was required to accomplish this phase of the analyses as was needed to make the ferrous/ferric routine work.

The first efforts to create solutions from the slags were based on the work of Matthes et al. (1983). The purported importance of this report lies in the use of a microwave oven as an aid in sample digestion, saving time and (according to the authors) allowing for more accurate results. A mixture of HCl, HF and HNO_3 (2.45:1.05:1.00, by volume of concentrated acid solution) was used by Matthes et al. to attack 0.5-1.0 grams of slag, and one to three minutes of microwave time helped the process along. Carbon dioxide was

used as a coolant before the samples were removed from the microwave, and the process was carried out in polycarbonate bottles which had proved best able to withstand the temperatures and pressures of the routine. Matthes et al. reported some leakage of acid vapor, but dismissed it as minimal.

Attempts to duplicate this procedure showed that not all slags are created equal. For starters, the minimal acid vapor leakage during microwavage in Matthes' experiments was anything but minimal in those from this work, despite Teflon seals around tightly-capped polycarbonate 85-ml. centrifuge tubes. In a few cases, samples were all but evaporated to dryness. It also developed early on that digestions of our slags were best carried out with no more than two or three drops of nitric acid; adding the 1.0 ml. recommended by Matthes et al. proved disastrous. As earlier suggested, the zirconia content of the slags was the most difficult to digest, and generally wasn't, despite the numerous acid combinations tried. The lead content proved more soluble in a HCl-HF mixture than expected, but a notable amount of CaO was found in energy dispersive X-ray (EDX) analysis of the undissolved material. The considerable Zr presence also found in this material suggests that the undissolved calcia was a part of small bits of crucible that accidentally found their way into the ground slag.

The procedure ultimately adopted used a sample size of 30-40 milligrams of slag, attacked with 3.5 ml. of a 7:3 mixture of HCl and HF (concentrated acids) and no more than two or three drops of concentrated HNO_3. Each digesting sample was sealed in the polycarbonate vials described above, and left alone for three to four days. A "master solution" was then made by diluting the resultant solution to 50 ml. with a 1.5% (saturated) boric acid

solution; the H_3BO_3 was one of the few recommendations adopted without alteration from Matthes et al. (1983). Each master solution could then be diluted as required for analysis by atomic absorption of the four dissolved elements (Pb, Fe, Ca and Si).

The analysis of the lead-silver alloys from the second set of slag equilibrations was much easier to accomplish, as both Pb and Ag are readily soluble in nitric acid. This alloy was usually found as a small button in the bottom of the quenched crucible after experiments. (Its weight, about .22 gm., was the first indication that Pb solubilities in the slags described in this work would be far less than first hypothesized.) To allay concern about anomalies in the analyses resulting from solidification segregation within the button, it was decided to use the entire sample in the analytical routine.

This routine began with the dissolution of the button in a mixture of 30 ml. of concentrated (70%) HNO_3 and 50 ml. distilled water. To facilitate digestion, each sample was heated for about one minute in the microwave, a technique that worked quite well. Upon the completion of dissolution, another "master solution" was made, this time by dilution to 250 ml. with distilled water. This solution could then be analyzed, again by atomic absorption, for Ag and Pb; since these were the only constituents of the alloy, this was sufficient to characterize the sample.

Some concern was evinced over a white precipitate that formed in the bottom of some of the samples after digestion. Although there is a limit to the solubility of lead nitrate, the amount of solution used should have been enough to ensure complete dissolution. One possible cause of the precipitate was the presence of small pieces of slag which remained stuck to the button;

these might have yielded such a material upon attack by nitric acid. The completion of the dilution to master solution-strength seemed to dissolve much of this precipitate.

CHAPTER 4

RESULTS

4.1 The Sample Labelling Scheme

In discussing the results of the various experiments, it is of some importance to first describe the identification label applied to the various experiments and the analytical materials derived from these experiments. As shall be seen, creating a system to keep samples readily identifiable was perhaps as complex a matter as any in the whole experimental regime.

The eventually-adopted sample identification label took the form A - BBBB - C - D - EE - FF - G. "A" represents the number 1, 2, or 3, signifying a pure metal, pure slag or "unseparated" (i. e., anything left over) material in the bottle so labeled. "BBBB" represents the month and date that the sample was quenched from the furnace (0112 for January 12, for example). Because several types of crucibles were used in the course of developing the experimental routine, "C" is used to identify the particular material (1 - fused silica, 2 - ZrO_2, 3 - graphite); "D" identifies a sample equilibrated over a nighttime period of about 14 hours (N) or a daytime period of ten hours (D).

"EE" describes the type of experiment and any gases used; the experimental routine finally adopted was described as "3E", the first-tried CO/CO_2 method as "1A". Last, and most important, were "FF" and "G". The former of these was the "shot-for" percentages of lead oxide in the final slag, as

taken from the work of Taskinen et al. (1984). As earlier mentioned, these were 15, 20 and 25% PbO; these same numbers were used in the Pb-Ag alloy equilibrations, despite the belief that the reduced a_{Pb} would decrease the lead oxide solubility accordingly. "C" was the initial calcia/silica ratio (0 - .40, 1 - .47, 2 - .57, 3 - .67, 4 - .10, 5 - .80).

As can be seen, the standardization of experimental procedure and equipment meant that a good deal of the labelling format was unnecessary; in fact, A - BBBB - D - FF - G was enough to distinguish any sample. This is the style that will be used in the remainder of this work, with the frequent dropping of "A" when it is obvious what type of sample (slag, metal, etc.) is being discussed.

4.2 The Lead Unit Activity Results

Table 3 shows the sample weights used for analysis of those slags equilibrated in contact with pure lead, i. e. with a_{Pb} equal to unity. This is shown for two reasons. Firstly, although it was hoped that 30 to 50 milligrams of material would be available for both the ferric/ferrous and Pb/Ca/Si/Fe analytical routines, the small amounts of material input sometimes rendered this impossible, as can be seen. Secondly, it allows for the introduction of a "Sample" number, 1 - 18, as a replacement for the labelling system described. (In other words, shorthand for a shorthand.) This will allow for more data per table instead of sample description.

Table 4 shows the results from the ferric/ferrous analysis, with the ratio shown as ferric/total iron after the work of Taskinen et al. (1984). These numbers, the first derived in the analytical portion of this research,

Table 3

Sample Weights for Pb Unit Activity Slags (mg)

Slag Label (2-)	Sample	AA	Fe^{2+}/Fe^{3+}
0311-D-15-0	1	37.7	44.5
0311-N-15-0	2	37.0	41.7
0330-D-15-1	3	36.2	40.6
0331-N-15-1	4	38.4	48.4
0303-D-15-2	5	41.9	34.7
0304-N-15-2	6	37.5	37.8
0212-D-20-0	7	20.6	20.8
0213-D-20-0	8	38.0	17.5
0119-D-20-1	9	41.6	38.1
0123-N-20-1	10	36.6	41.7
0128-N-20-2	11	34.5	37.8
0129-N-20-2	12	43.4	37.2
0312-N-25-0	13	12.2	20.0
0314-N-25-0	14	28.2	31.5
0402-D-25-1	15	32.0	44.3
0402-N-25-1	16	34.6	36.4
0403-D-25-2	17	34.7	48.4
0403-N-25-2	18	32.5	30.4
0717-N-15-4	19	39.6	28.3
0718-N-20-4	20	21.4	14.2
0719-N-25-4	21	44.6	23.4
0722-N-15-5	22	38.0	37.4
0723-N-20-5	23	45.3	36.1
0725-N-20-5	24	37.6	34.7
0724-N-25-5	25	41.7	34.0

Table 4

Ferric/Ferrous Iron Analyses, Pb Unit Activity Slags

Sample	Fe^{3+}/Total Fe	Wt.-% Fe
1	.102	24.0
2	.087	23.3
3	.087	24.7
4	.073	19.5
5	.139	24.5
6	.157	24.4
7	.116	22.8
8	.108	22.4
9	.113	22.2
10	.274	21.8
11	.142	20.9
12	.224	21.4
13	.111	25.8
14	.172	28.2
15	.186	23.5
16	.190	24.1
17	.250	22.7
18	.312	25.5
19	.065	24.7
20	.125	23.2
21	.220	22.6
22	.148	29.3
23	.096	19.3
24	.182	25.8
25	.268	23.9

were also the first to indicate that the overall results of this research would be considerably different from those of the Finnish group, as they are considerably lower than the ratios in the "FeO"/Fe_2O_3 mixture used to make up the charges for equilibration. At the same time, these results also provided some gratification in the knowledge that the sealed-ampule method of testing had performed as planned.

Table 5 displays the results of the atomic absorption analyses for these slags, and some discussion of each column is useful. It should first be noted that the total iron percentages from the AA are significantly higher than those derived from the spectrophotometric method; in fact, they average 5.71% Fe higher. The answer to the obvious questions arising from this discrepancy is that the AA numbers should be considered more trustworthy, as the analytical routine for this method required the digestion of the entire sample. The HCl used in the spectrophotometric method certainly did not dissolve the entire slag sample, and quite conceivably may not have penetrated the silicate matrix to the degree necessary to reach and thus dissolve all the iron. Better grinding of the slag might have yielded improved results in this regard, but at the increased risk of Fe^{2+} oxidation, and the latter was of greater concern. Some concern might also be expressed in this matter as to whether the ferrous or ferric iron content in a slag is more prone to selective "liberation" from the matrix, and whether such a variance might have affected the analytical results. In fact, a linear regression of the difference between the AA and spectrophotometric total iron percentages versus the ferric/total iron ratio for the 18 analyses shows a correlation coefficient of -.030, a demonstration of almost perfect scatter. This suggests that the

Table 5

Pb Unit Activity Slag AA Analyses (Wt.-%)

Sample	Iron	Silicon	Calcium	Lead
1	29.31	13.67	10.25	4.05
2	26.28	13.86	13.65	2.57
3	26.66	12.98	11.84	4.49
4	36.65	15.36	13.02	3.18
5	28.58	12.77	11.69	6.87
6	27.73	14.34	13.47	4.81
7	28.76	13.85	11.23	5.15
8	29.08	12.44	11.78	4.05
9	31.01	13.89	10.88	9.93
10	28.76	11.40	10.96	13.07
11	24.49	12.57	10.80	7.06
12	24.77	12.08	10.86	8.25
13	35.66	13.84	13.11	4.02
14	27.22	12.04	10.55	7.11
15	30.08	12.87	10.47	12.34
16	29.99	12.48	11.05	11.08
17	28.75	11.44	10.73	14.01
18	31.23	9.72	9.73	14.31
19	27.90	15.81	11.87	4.48
20	26.64	14.32	11.97	14.25
21	21.80	13.96	9.42	24.30
22	31.78	14.47	14.05	4.81
23	28.81	14.21	13.27	8.80
24	29.26	13.26	12.93	10.05
25	27.82	12.48	12.62	13.49

concern over the possibility of ion-selective iron dissolution in the spectrophotometric analyses may safely be eschewed.

The silicon results are somewhat open to question, as Si AA analyses by their very nature are usually "noisy," and thus subject to large deviations. In fact, those in Table 5 are notable in that they are a good deal less noisy than usual; the average standard deviation of the readings is only 2.42%. The SiO_2 percentages are about 1% less than originally added to the slag, a result attributable to the dissolution in the slags of zirconia from the crucible. The calcium analyses are much more stable (as expected), but it should be noted that SiO_2 often interferes with Ca atomic absorption. The use of a higher-temperature nitrous oxide-acetylene flame was the means chosen to deal with this potential interference.

It is notable that the lead contents of the slags are considerably less than those predicted in calculating the initial reagent charges. Even conversion of the lead percentages shown in Table 5 to %PbO leaves them far short of the 15, 20 and 25 percent originally "shot for." Unfortunately, this was discovered only after the slags containing Pb-Ag alloys had been equilibrated; otherwise, a higher initial lead activity that the .25 chosen for this second set of experiments would have been used.

Table 6 lists a variety of statistics calculated from the analytical results of Table 5. The calcia/silica ratio has previously been discussed, and mention has also been made of the iron/silica ratio as a controllable degree of freedom in the experimental system. The "percent ZrO_2" calculation requires the use of the ferric/total iron ratios listed in Table 4 to derive the percentages of FeO and Fe_2O_3 in the slag. The zirconia level is then merely

Table 6

"Vital Statistics" - Pb Unit Activity Slags

Sample	Calcia/Silica	Iron/Silica	Wt.-% "Zirconia"
1	.49	1.002	13.95
2	.64	.886	14.35
3	.60	.960	16.10
4	.55	1.115	-2.15
5	.60	1.045	11.63
6	.62	.904	8.97
7	.53	.970	11.66
8	.62	1.093	14.64
9	.51	1.043	4.01
10	.63	1.179	8.10
11	.56	.910	18.43
12	.59	.959	17.45
13	.62	1.203	1.29
14	.57	1.056	16.07
15	.53	1.093	4.91
16	.58	1.123	6.55
17	.62	1.174	7.47
18	.65	1.502	8.66
19	.49	.825	8.60
20	.55	.869	2.51
21	.44	.730	2.04
22	.63	1.027	2.66
23	.61	.948	4.10
24	.64	1.032	4.32
25	.66	1.042	4.25

equal to 100 percent minus the weight percentages of SiO_2, CaO, PbO, FeO and Fe_2O_3. It is thus merely an empirical figure; however, the average of 10.11% ZrO_2 is reasonably close to the 7% claimed by Taskinen et al. (1984).

4.3 The Pb-Ag Alloy Slag Results

Table 7 shows in similar fashion to Table 4 the sample weights for the 18 slags equilibrated in contact with a Pb-Ag alloy. More material was generally recovered for analysis from these experiments, and thus the sample weights were more consistent. The differences between iron analyses from the previous set of slags (discussed above) led to the use of somewhat lower sample weights, in the hope that the digestion would be more complete, making the spectrophotometric results closer to the actual (AA) iron percentages.

Table 8 lists the results of the ferric/ferrous analyses. One result, that of Sample 6, is immediately a source of suspicion, given the results for the slags of the first set and the others of this one. This anomaly can be tied to the lack of recovery of a Pb-Ag alloy button from the crucible; apparently the metal was never added in the first place. Such a lack of metal would cause any excess oxygen in the equilibrating system to be 'used up' in oxidising ferrous iron to ferric, resulting in the high ferric/total iron reading. For statistical purposes, this result was discarded.

Table 9 displays the results of the AA analyses, again in similar fashion to those of the Pb unit activity slags. The obvious difference between the two data sets lies in the percentages of lead; it is certainly no surprise that the alloy slag Pb contents are considerably reduced. Another item of note in

Table 7

Sample Weights From Pb-Ag Alloy Slags (mg)

Slag Label (2-)	Sample	AA	Fe^{3+}/Fe^{2+}
0513-D-15-0	1	33.0	38.0
0513-N-15-0	2	38.6	36.0
0514-D-15-1	3	33.2	42.0
0514-N-15-1	4	33.6	39.7
0515-D-15-2	5	32.5	30.4
0515-N-15-2	6	38.5	36.4
0516-D-20-0	7	36.2	33.5
0516-N-20-0	8	36.5	46.0
0517-D-20-1	9	36.7	40.8
0517-N-20-1	10	34.4	39.2
0518-D-20-2	11	26.1	40.6
0518-N-20-2	12	34.6	32.9
0519-D-25-0	13	25.2	36.4
0519-N-25-0	14	29.0	35.5
0520-D-25-1	15	36.9	35.4
0520-N-25-1	16	28.3	35.8
0521-D-25-2	17	25.5	37.1
0521-N-25-2	18	32.4	34.4

Table 8

Ferric/Ferrous Analyses, Pb-Ag Alloy Slags

Sample	Fe^{+3}/Total Fe	Percent Fe
1	.038	28.01
2	.085	26.93
3	.048	24.68
4	.110	25.61
5	.129	25.62
6	.978	26.85
7	.049	25.74
8	.105	28.27
9	.104	26.62
10	.132	19.83
11	.130	26.59
12	.152	25.67
13	.104	22.80
14	.138	27.15
15	.137	25.94
16	.146	26.36
17	.169	24.78
18	.179	28.18

Table 9

Atomic Absorption Analyses, Pb-Ag Alloy Slags (%)

Sample	Iron	Silicon	Calcium	Lead
1	28.71	13.86	10.26	.91
2	28.04	13.69	9.78	.61
3	27.79	14.41	11.07	1.09
4	27.38	14.08	12.72	.97
5	28.00	13.11	10.61	1.36
6	28.44	13.10	12.76	1.11
7	30.32	13.72	10.63	1.52
8	29.66	13.58	12.54	1.31
9	25.61	14.47	10.22	1.89
10	28.13	13.36	11.16	1.57
11	28.64	14.48	12.31	2.33
12	27.10	11.68	10.91	1.87
13	24.80	14.70	11.31	3.71
14	29.14	14.21	10.99	1.45
15	27.71	14.25	9.89	2.45
16	23.23	11.78	9.46	2.19
17	32.06	13.53	12.45	3.13
18	27.08	12.84	11.42	1.54

comparing Tables 6 and 9 is that the variance between the iron analyses as discussed above now only averages 1.82%; the relatively smaller sample sizes may account for this. Table 10 shows the CaO/SiO_2, Fe/SiO_2, and "percent ZrO_2" in the same manner as Table 7.

The analyses of the lead-silver alloys shown as Table 11 demonstrate that it is possible at times to get considerably different results from the same material with different analytical methods. The first column in this table shows the "analytical" result from knowing only the weight of the alloy button. If one presumes silver to have been insoluble in the slag, a supportable suggestion (Richardson and Billington, 1956), then the difference between the button weight and the amount of Ag originally added must have been lead. While a minute amount of slag adhered to the buttons as they were weighed, it may be safely be considered negligible in comparison to the calculated lead weight.

The second column of Table 11 shows the lead percentage of the button achieved by AA analysis of the solution made from the button (as described in Chapter Three) for silver - the difference being lead - and the third column represents the Pb percentage derived from the AA analysis of this solution for lead. The fourth column uses both of these analyses, by normalizing the percentages of Ag and Pb against a total of 100. In no case do any of these types of analyses agree well with another over all 18 samples, leaving open the question of which one would be the most appropriate for further use.

The ultimate winner of this analytical "beauty contest" was the weight difference method (column 1 in Table 11), since it appeared the most likely to minimize analytical error. Since there was no button available from sample

Table 10

"Vital Statistics" - Pb-Ag Alloy Slags

Sample	Calcia/Silica	Iron/Silica	Pct. "Zirconia"
1	.485	.969	17.92
2	.513	.958	18.45
3	.502	.902	16.56
4	.591	.909	15.38
5	.529	.999	19.10
6	.637	1.015	12.35
7	.507	1.033	14.91
8	.604	1.021	13.40
9	.462	.828	19.37
10	.546	.985	17.40
11	.556	.925	11.91
12	.612	1.085	22.28
13	.503	.788	16.45
14	.506	.959	14.60
15	.454	.909	16.84
16	.525	.922	28.84
17	.602	1.108	8.25
18	.582	.987	16.24

Table 11

Comparison of Methods, Pb-Ag Alloy Analysis (% Pb)

Sample	Sample Wt.	AA - Ag	AA - Pb	AA - Normalized
1	33.96	18.65	37.96	31.82
2	4.67	19.26	36.79	31.30
3	34.23	16.17	36.44	30.30
4	32.26	14.23	33.41	28.03
5	32.25	18.49	34.25	29.59
6	-----	-----	-----	-----
7	1.20	31.29	32.42	32.06
8	35.06	18.70	33.17	28.98
9	34.45	13.46	38.77	30.94
10	35.39	19.06	36.73	31.20
11	33.61	33.10	27.57	29.18
12	27.29	16.17	32.74	28.09
13	31.88	34.62	23.10	26.11
14	37.05	21.53	35.41	31.09
15	34.33	25.53	29.27	28.21
16	34.30	16.21	36.33	30.24
17	33.62	67.54	22.80	41.26
18	36.14	44.04	22.88	29.02

6, there was obviously no result which could be used. In addition, the button weight from sample 7 seemed anomalous, especially in comparsion with the AA analyses; the data from this slag was also discerned. This left 41 total slag analyses for further consideration, perhaps not too great a concern in light of the considerable experimental and analytical challenges that had been met in reaching this point.

As might be recalled, the reason for equilibrating slags in contact with the Pb-Ag alloys in the first place was to lower the PbO solubility by reducing a_{Pb}. The data compiled by Hollitt (1984b) was used as the source of Pb activity values. Of course, Hollitt's data was not compiled at the exact lead percentages of the alloys in this study; therefore a method was needed for accurately interpolating between his data points. Such a method is the subregular solution model first proposed by H. K. Hardy and expanded upon by Lupis (p. 178). The subregular model is expressed through the equation,

$$RT \ln \gamma_1 = X_2^2 [2X_1 A_{21} + (1 - 2X_1) A_{12} + X_1 (2 - 3X_1) A_{22}], \quad (1)$$

where the subscripts 1 and 2 represent the components in a binary system, γ is a component's activity coefficient, X the appropriate mole fraction and A an empirically-determined subregular interaction coefficient. A curve-fit using Hollitt's activities and mole fractions found A_{Pb-Ag} at 1200°C equal to 1465.92, A_{Ag-Pb} 2834.98, and A_{Ag-Ag} -2014.55. Since

$$a_{Pb} = \gamma_{Pb} X_{Pb}, \quad (2)$$

using these interaction coefficients allowed the calculation of γ_{Pb}, and thus a_{Pb} for the various lead percentages in this study. Furthermore, knowing a_{Pb} allowed for the calculation of a "corrected" percentage of Pb in the slag, equal to the actual level divided by the lead activity in the alloy. Table 12 shows γ_{Pb}, a_{Pb} and this corrected lead level (expressed as % PbO, by multiplying the %Pb by the molecular weight of PbO, divided by the molecular weight of Pb) for the 16 usable Pb-Ag alloy slags.

Table 12

Pb Activities and "Corrected" PbO in the Pb-Ag Alloy Slags

Sample	X_{Pb}	γ_{Pb}	a_{Pb}	"% PbO"
1	.211	1.365	.288	3.40
2	.217	1.359	.295	2.24
3	.213	1.362	.290	4.03
4	.199	1.372	.273	3.81
5	.199	1.372	.273	5.38
8	.219	1.361	.298	4.73
9	.219	1.361	.298	6.85
10	.222	1.356	.301	5.61
11	.209	1.368	.286	8.78
12	.163	1.405	.229	8.78
13	.196	1.378	.270	14.81
14	.235	1.349	.317	4.92
15	.214	1.364	.292	9.04
16	.214	1.364	.292	8.08
17	.209	1.368	.286	11.78
18	.228	1.355	.309	5.37

CHAPTER 5

DISCUSSION OF RESULTS

5.1 The Empirical Model

As mentioned earlier, there are two forms of soluble lead in blast-furnace slags. The first of these is "neutral" or reduced lead, which dissolves as a result of the simple reaction,

$$Pb(m) = Pb(s) \qquad (2)$$

where the *denotants* m and s represent the metallic and slag phases in equilibrium, respectively. As can be seen, this reaction requires no oxygen, and is thus largely independent of the system's oxygen pressure, aside from any effects which p_{O_2} may have on the activity coefficient of Pb(s). The presence of neutral lead in slags is generally limited to about .1 percent, although some studies have suggested higher values (Meyer and Richardson, 1957; Meyer et al., 1966; Saito, 1957).

The other form of lead in slag is "oxidic" lead, or dissolved PbO. This is created by the reaction,

$$Pb(m) + \frac{1}{2} O_2 = PbO(s) \qquad (3)$$

which the reader will see as being clearly affected by the system oxygen pressure. Specifically, Eq. 3 is subject to a temperature-dependent equilibrium constant K, where

$$K_3 = \frac{a_{PbO}}{\sqrt{p_{O_2}}\, a_{Pb}} \tag{4}$$

If a_{Pb} is set equal to unity (as is the case in the lead blast furnace), then $a_{Pb}/\sqrt{p_{O_2}}$ is equal to K_3. The activity of PbO is of course equal to the lead oxide mole fraction (X_{PbO}) times its activity coefficient (γ_{PbO}), so

$$K_3 = \frac{X_{PbO}\, \gamma_{PbO}}{\sqrt{p_{O_2}}} \tag{5}$$

Knowing three of the four variables in this equation obviously makes the fourth a known as well.

The total lead in solution in a slag is thus the combined levels of neutral and oxidic Pb; but in most slags the preponderance is certainly oxidic. Saito (1957) has reported that this preponderance changes at p_{O_2} values below 10^{-9}, although the relationship nevertheless remains dependent on p_{O_2}. This type of change in species predominance is not unusual in slag systems; it has also been noticed with Sb, As and other trace metals (Matyas, 1975). The reader will notice from Tables 5 and 9 that the Pb percentages in

the slags from this investigation are considerably above .1, and it will be assumed that for all practical purposes that all of the lead in these slags is oxidic.

Rearranging Eq. 5, yields

$$\log K_3 = \log X_{PbO} + \log \gamma_{PbO} - \frac{1}{2} \log p_{O_2} \qquad (6),$$

and further rearrangement shows that

$$\log p_{O_2} = 2 \log X_{PbO} + 2 \log \gamma_{PbO} - 2 \log K_3 \qquad (7)$$

This last rearrangement is presented because the experimental procedure for the work presented here did not allow for the measurement of p_{O_2}, a parameter of obvious importance in the consideration of lead blast-furnace equilibria. A means of calculating it would be of considerable utility.

This could of course be done if γ_{PbO} were known; therefore, the development of a model for expressing γ_{PbO} as a function of the various slag chemistry parameters would solve the challenge posed by Eq. 7. Figures 6 and 7, taken from the work of Taskinen et al. (1984), yield the necessary data for the development of such a model; specifically, this data is made available in the form of the points formed by the intersections of the iso-calcia/silica and iso-p_{O_2} lines in these graphs. (The reader will ask why the f_{PbO} values that make up the y-axis of Figs. 6 and 7 aren't usable, since they are in fact the same as γ_{PbO}. Actually, they are; but the "intersection points" involved one less interpolated value, and it was felt that this would prove more accu-

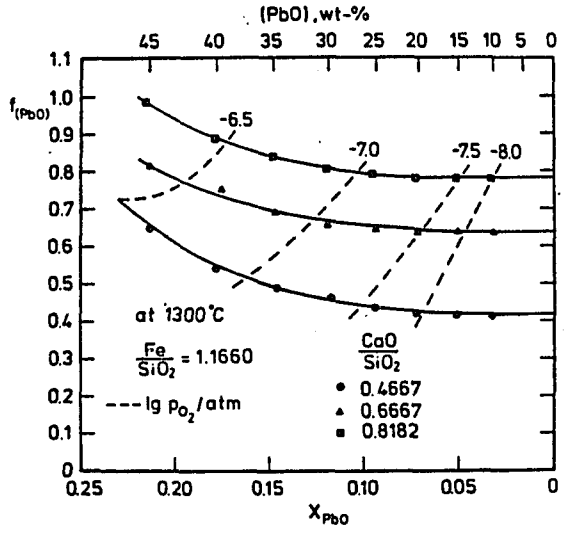

Fig. 6. Figure 9 from Taskinen et al. (1984), showing PbO activity coefficients and oxygen isobars as a function of PbO mole fraction and calcia/silica ratio at constant Fe/Si ratio of 1.1660.

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rate. The use of Taskinen et al.'s data in this study is not entirely without hazard, anyway; see Appendix C for a more complete discussion.)

What the points collected from the use of Figs. 6 and 7 demonstrate is that γ_{PbO} is affected by both the calcia/silica and iron/silica ratios of a slag system such as this. Taskinen et al. made no attempt to express this as a mathematical function, but the availability to the author of curve-fitting software developed by the SAS Institute of Cary, North Carolina allowed him to do so for himself. As Lupis (1983, p. 164) points out, the logarithm of the activity coefficient of a species in dilute solution is closely related to its mole fraction, so such a function would include X_{PbO} as one of its terms. Other terms could be included with an empirically-determined combination of

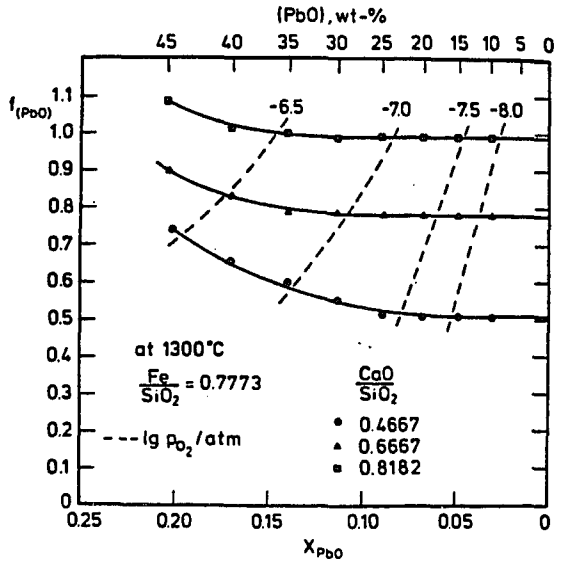

Fig. 7. Figure 11 from Taskinen et al. (1984), similar to Fig. 6 but with Fe/Si ratio of .7773.

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possibilities involving CaO/SiO_2 and Fe/SiO_2; so a series of such possibilities were curve-fit in combination with X_{PbO} to yield the one with the best correlation to the data points derived from Taskinen et. al's work. This "optimized" function turned out to be

$$\log \gamma_{PbO} = .64\, X_{PbO} + .76F^G - .10 \log F - .78, \qquad (8)$$

with F and G being the calcia/silica and iron/silica weight ratios, respectively. Plugging these back into Eq. 7 yields:

$$\log p_{O_2} = 2 \log X_{PbO} + 1.28\, X_{PbO} + 1.52\, F^G - .20 \log F - 1.55 - 2 \log K_3 \qquad (9)$$

The reader may recall that the work of Taskinen et al. (1984) from which Eq. 9 was derived was done at 1300°C, and wonder how its use at 1200°C can be justified. K_3 is of course easily translatable, being nothing more than a function of temperature; but the expression for log γ_{PbO} developed as Eq. 8 is in fact valid only at the higher temperature. However, other work (Meyer et al., 1966) has shown that γ_{PbO} changes very little as a function of temperature in the range being discussed, so it seems reasonably safe to use Eq. 8 as at least a reasonable approximation of log γ_{PbO}, even at 1200°C.

Table 13 lists the log p_{O_2} values calculated for the slags equilibrated in this work, and Fig. 8 shows them plotted against log X_{PbO}. Figure 8 vindicates to a degree the approach of using Eq. 8, as the regression line slope (.948) is very close to the 1.0 value which one would predict from Eq. 6. It will also be noted that the dependency of X_{PbO} on p_{O_2} at these oxygen pressures is extremely strong; a reexamination of Figs. 6 and 7 shows that such is not the case at higher p_{O_2} values, as the O_2 isobars increasingly deviate from the vertical (i. e., lose association with constant X_{PbO}).

Figure 9, also taken from the work of Taskinen et al. (1984), shows a different dependency which gains importance at higher p_{O_2} values, namely that of PbO weight percent (which is of course closely related to X_{PbO}) on the ferric/total iron ratio. The ferric/ferrous iron ratio and slag lead oxide contents are related by

$$2FeO_{1.5(s)} + Pb(m) = 2FeO(s) + PbO(s) \qquad (10)$$

Table 13

Calculated p_{O_2} Values, From Eq. 9

Pb Unit Activity Slags		Pb-Ag Alloy Slags	
Slag	Log $p_{(O_2)}$	Slag	Log $p_{(O_2)}$
1	-10.119	1	-10.320
2	-10.283	2	-10.629
3	-9.834	3	-10.137
4	-10.458	4	-10.090
5	-9.518	5	-9.961
6	-9.800	8	-9.944
7	-9.856	9	-9.648
8	-9.970	10	-9.809
9	-9.363	11	-9.428
10	-8.924	12	-9.308
11	-9.415	13	-8.910
12	-9.258	14	-10.002
13	-10.148	15	-9.479
14	-9.481	16	-9.328
15	-9.129	17	-9.206
16	-9.163	18	-9.783
17	-8.871		
18	-8.888		
19	-9.997		
20	-8.889		
21	-8.361		
22	-9.886		
23	-9.307		
24	-9.170		
25	-8.842		

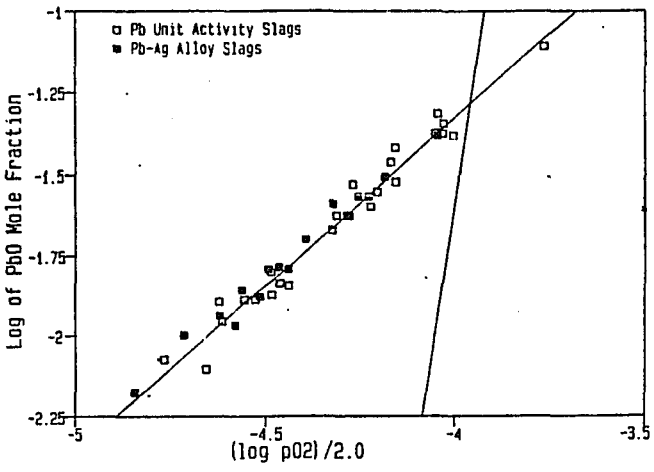

Fig. 8. PbO mole fraction vs. oxygen partial pressures calculated with Eq. 9, experimental slags. The "stray" line is adapted from the regression line in Fig. 9(I) of Saito (1957).

If a_{Pb} is set equal to unity, then equilibrium constant K_{10} can be expressed as:

$$K_{10} = \frac{a_{FeO}^2 \, a_{PbO}}{a_{FeO_{1.5}}^2} \qquad (11)$$

Equation 11 suggests that the amount of PbO in a slag can be directly related to the relative amount of ferric and ferrous iron, if the activity coefficients of the latter are relatively unaffected by changing calcia/silica and iron/silica ratios.

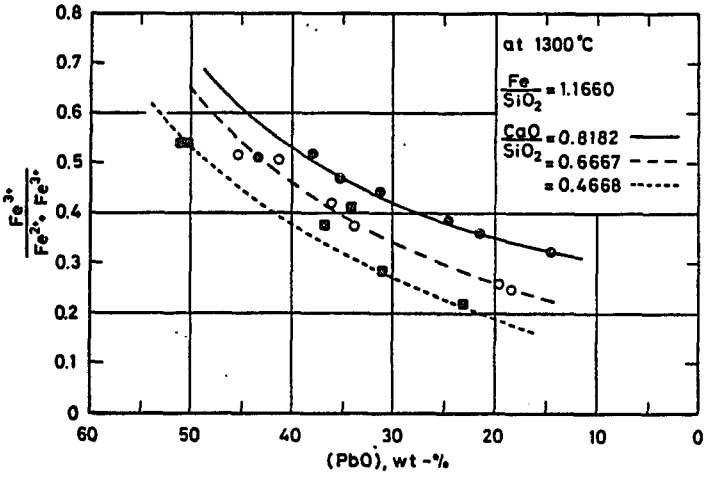

Fig. 9. Figure 4 from the work of Taskinen et al. (1984), showing ferric/total iron ratio as a function of PbO mole fraction and calcia/silica ratio at a constant Fe/Si ratio.

Figure 10 shows that such a relationship would be overstated in this case. The relatively poor correlation of the regression line in this graph (compared with that in Fig. 8) instead furthers the suggestion from Fig. 9 that the dependency of X_{PbO} on the relative amounts of ferric and ferrous iron decreases with decreasing p_{O_2} values. This is no surprise, as the work of Goel and Kellogg (1984) shows how changing Fe/(CaO + SiO_2) and CaO/SiO_2 ratios can change the ferric/ferrous iron ratio at constant oxygen pressures. Figure 11 shows that a similar effect was observed in the results from this study.

While Eq. 9 is certainly a useful tool for predicting slag equilibria, it does have drawbacks which deserve discussion. The first of these is the

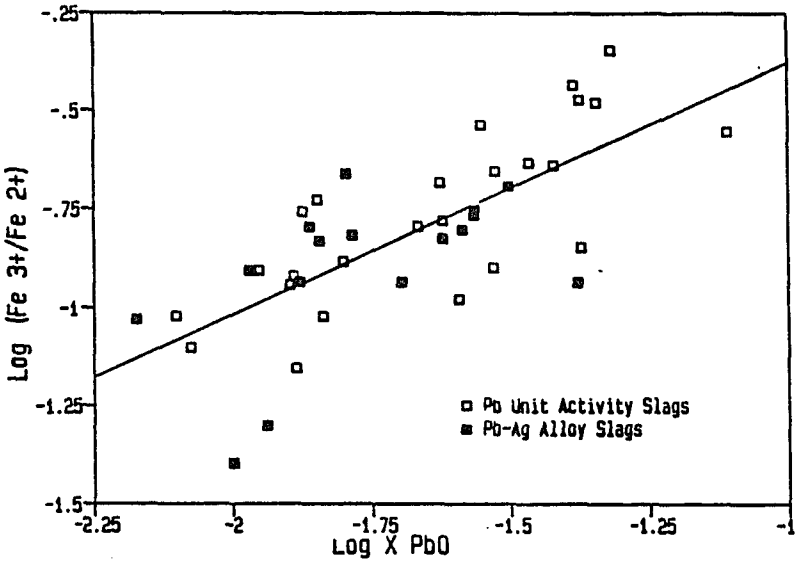

Fig. 10. PbO contents in experimental slags as a function of ferric/ferrous ratio.

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empirical nature of Eq. 8, which has little relationship to the structural or chemical properties of a multi-component molten oxide system. Secondly, it should be pointed out that the use of Eq. 9 is essentially an extrapolation to p_{O_2} values outside the range used by Taskinen et al. (1984), with all the inherent "questionability" associated with such usage. Lastly, the reader will recall from Chapter 1 that most actual blast-furnace slags contain considerably more than PbO, CaO, SiO_2 and FeO_x; a model such as Eq. 9 which makes no allowance for other oxide (and possibly sulfide) components has at best limited utility. There are models, however, which are possibly capable of meeting these objections, and it is to best of these models, that developed by Hollitt (1984a,b), to which this discussion will now turn.

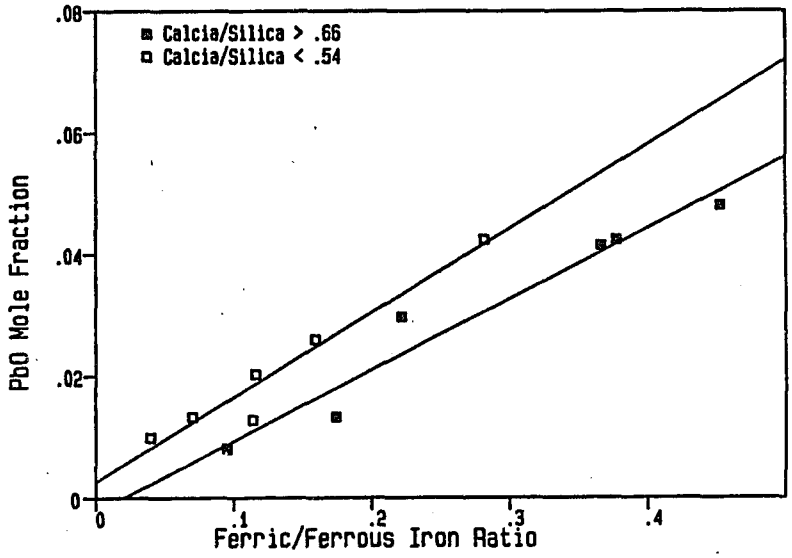

Fig. 11. PbO contents of experimental slags as a function of ferric/ferrous ratio, showing effect of calcia/silica ratio variance.

5.2 Hollitt's Model

5.2.1 Acids, Bases and Others

It was earlier mentioned that a slag is defined as a mixture of silicate polyions of varying length, with its properties being determined to a large extent by the length and type of those polyions. In turn, the nature of the polyions is determined by the chemical composition of the slag, specifically the type of oxides added to the SiO_2 that forms its base. Figure 12, taken from the work of Masson (1972), shows a "typical" silicate polyion; the oxygen atoms which bind it together are called "bridging" oxygen atoms, and they are the key in the development of most slag thermodynamic models.

Figure 13, from the work of Lin and Pelton (1979), shows what happens to a "bridge" upon the addition of a basic oxide, such as PbO. The bridge

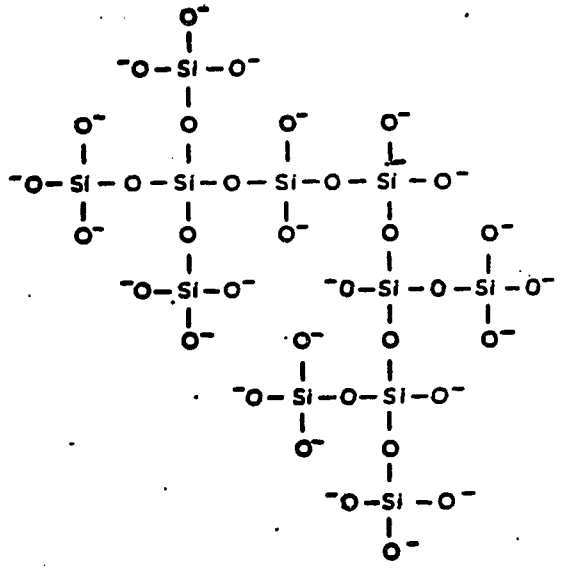

Fig. 12. Figure 1 from Masson (1972), showing a "typical" silicate polyion.

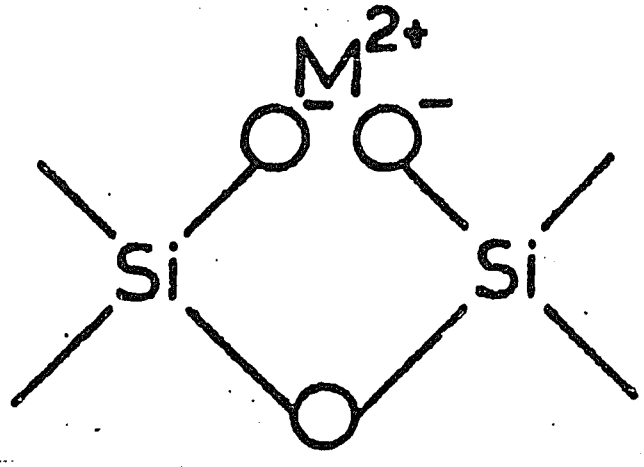

Fig. 13. Figure 1 from Lin and Pelton (1979), showing the effect on a silicate polyion of a "broken bridge."

breakage can be represented as a chemical equilibrium:

$$O^{o} + O^{2-} = 2O^{-}, \qquad (12)$$

In this representation, O^o represents a "bridging" oxygen ion (bound to two silicon atoms), O^{2-} is a "free" divalent oxygen ion (that introduced with the basic cation), and O^- is an oxygen bound to one silicon atom and to the cation (as shown in Fig. 13). The "basicity" of an oxide is the degree to which it will cause such bridge breakage upon its addition to a system containing a molten acidic oxide, such as silica. In general, monovalent and divalent cations form the most basic oxides, tetravalent cations form acidic oxides (those which form polyions), and trivalent oxides ($FeO_{1.5}$ and $AlO_{1.5}$, for example) are amphoteric, capable of basic or acidic behavior depending on the conditions.

Several studies on the system $PbO-MO-SiO_2$, where MO is another divalent oxide, have shown that PbO is roughly in the middle of the range of MO basicities. BaO, CaO and MgO are much more basic; ZnO can be more or less basic, depending on the amount of SiO_2 in the system; and CoO, FeO, and NiO are always less basic (Meyer et al., 1966; Ouchi and Kato, 1983; Richardson and Pillay, 1961; Sugimoto and Kozuka, 1978; Taskinen et al., 1982; Taskinen et al., 1984). Since the addition of a less basic oxide to a $PbO-SiO_2$ melt decreases a_{PbO}, and the addition of a more basic oxide increases it, the question of relative basicities becomes of obvious importance in the development of any slag thermodynamic model.

Equation 12 applies, of course, only when there are bridges left to break, i. e. when the ratio of basic oxides to silica is less than two. This is the case in most traditional slag compostions, and so the effect on the number of O^- ions caused by the addition of one mole of basic oxide to a

"polymerized" melt can be quantitized as:

$$\frac{\partial n_{O^-}}{\partial n_{MO}} = 2 \tag{13}$$

The number of O^o ions is accordingly decreased:

$$\frac{\partial n_{O^o}}{\partial n_{MO}} = -1 \tag{14}$$

However, there were no free oxygen radicals in the molten slag when MO was added, so

$$\frac{\partial n_{O^{2-}}}{\partial n_{MO}} = 0, \text{ when } \frac{X_{MO}}{X_{SiO_2}} \leq 2 \tag{15}$$

These relationship bring us back to the question of how the less basic and amphoteric oxides behave in this structure, especially as the MO/SiO_2 ratio approaches two. One way of making such a determination is to assess the effect oxide additions have on a molten oxide system's viscosity; the breaking up of polyions is accompanied by a decrease in this parameter. Figure 14, taken from the work of Richardson, demonstrates this effect in the alumina-calcia-silica system at 1900°C; Al_2O_3 at high CaO/SiO_2 ratios causes a viscosity increase, while causing a reduction at more acidic compositions. The reader will notice that at some "in-between" compositions, the effect is less clear, and that the amount of alumina itself has an effect on

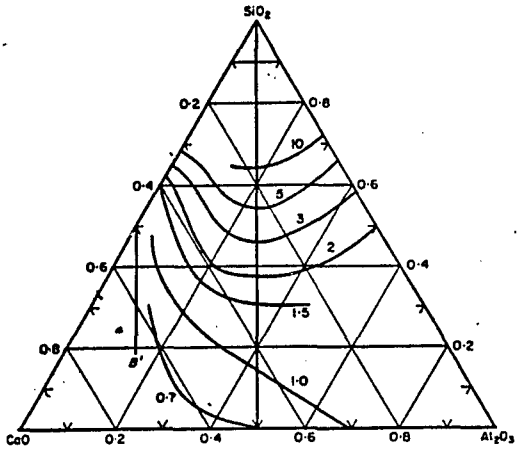

Fig. 14. Isoviscosity lines in the molten calcia/alumina/silica system at 1900°C, from Richardson (1974), p. 107. The addition of basic oxides lowers viscosities in a primarily silicate melt.

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how further additions affect the viscosity. In some cases, this relatively "neutral" behavior is taken on by less basic divalent oxides; Hollitt et al. (1984a,b) have claimed that FeO often remains coordinated by O^{2-} in even highly acidic slags, rather than participating in bridge-breaking. $FeO_{1.5}$ is acidic enough in certain circumstances to actually form polyions, and in fact is the basis of a new class of slags, the "calcium ferrite" type. When an amphoteric oxide engages in acidic behavior, it "uses up" .5 moles of MO to form the equivalent of a mole of tetravalent oxide:

$$Fe^{3+} + \frac{1}{2} M^{2+} \equiv Si^{4+} \qquad (16)$$

Hollitt (1984a) teaches that such behavior on the part of amphoteric oxides is

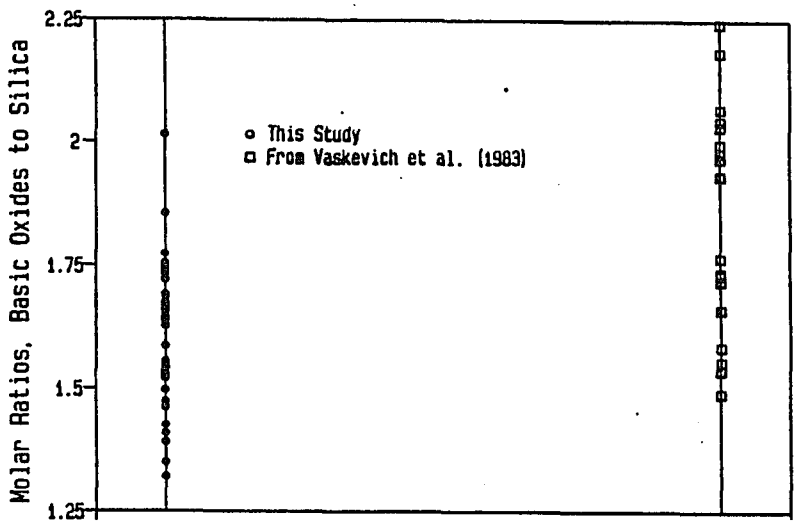

Fig. 15. A histogram showing the molar ratios of basic oxides to silica, from the experimental slags (left), and those of Vaskevich et al. (1983, right).

the rule rather than the exception in slags where MO/SiO_2 is less than two. Figure 15 shows that these are the types of slags equilibrated in both this investigation and that of Vaskevich et al. (1983), so the assumption will be gone along with for now.

5.2.2 Thermodynamics of Mixing in Slag Systems

In continuing this discussion of how the atomic structure of molten slags has been related to the thermodynamic properties of their constituents, it is useful at this time to introduce some new terms of importance. First of these is n_O, the number of moles of adjacent bridge/bridge breakage posi-

tions in the quasilattice that makes up the structure of molten silicates. Hollitt (1984a) developed an equation representing $n_{\underline{O}}$ as a function of other slag parameters:

$$n_{\underline{O}} = \frac{3n_{O^-}\left(2n_{Si} - \frac{n_{O^-}}{2}\right)}{2\,(n_{Si} + n_{O^{2-}})\,e^{B}} \qquad (17)$$

The oxygen ion terms have been seen before; n_{Si} is the number of SiO_2 molecules, and B is a temperature-dependent term related to the energy associated with the pairing of a broken bridge with a non-broken bridge. The e^B term is included to reflect the reduced chances of such a pairing, as it would increase the energy state of the system.

If one uses the assumptions made by Hollitt (acidic behavior of amphoteric oxides, O^{2-} coordination of FeO, and MO/SiO_2 ratios less than two), then the oxygen ion concentrations can be mathematically expressed as a function of the slag chemistry:

$$n_{O^{2-}} = n_{FeO} - .5\, n_{FeO_{1.5}} \qquad (18)$$

$$n_{O^-} = 2\,(n_{PbO} + n_{CaO}) \qquad (19)$$

$$n_{Oo} = n_{PbO} + 2\, n_{SiO_2} + n_{CaO} - n_{O^-} \qquad (20)$$

The n's can, of course, be replaced by mole fractions for a system with a total number of molecules (SiO_2 + PbO + CaO + FeO + $FeO_{1.5}$) equal to Avogadro's

number. Additional components can be put into Eqs. 18-20 as their mode of behavior in the slag structure would warrant. Since it has been decided that the amphoteric oxides will be acidic in this case, n_{Si} must also be redefined:

$$n'_{Si} = n_{SiO_2} + .5\, n_{FeO_{1.5}} \qquad (21)$$

Another term that needs introduction is ΔG^o_O. This term represents the free energy of mixing one mole of bridge-breaking material into a molten oxide to produce a completely "depolymerized" molten oxide system; i. e., one with no silicate polyions at all. The employment of ΔG^o_O does not, however, account for the free energy change from the distortion of the quasilattice which this addition of basic oxide causes, and such a term is required in the development of a model. (Thus the presence of e^B in Eq. 17.) As might be suspected, ΔG^o_O is related to the free energy of formation of a pure divalent metal subsilicate (such as Pb_2SiO_4); the relationship developed by Hollitt (1984b) is shown as Fig. 16. The reader should note that the relationship shown in Fig. 16 is independent of the cation being considered.

The entropy of mixing basic oxide into a silicate melt also merits consideration. Lin and Pelton (1979) have shown that this entropy is primarily the result of configurational considerations, thus making it necessary to evaluate only ΔS^M_C, the configurational entropy of mixing. This term is related to the number of ways that the free oxygen radicals and silicon atoms in a slag can be distributed over the available sites in the quasilattice. Lin and Pelton expressed this as the product of two multiplicities, the first in the case of complete bridge breakage:

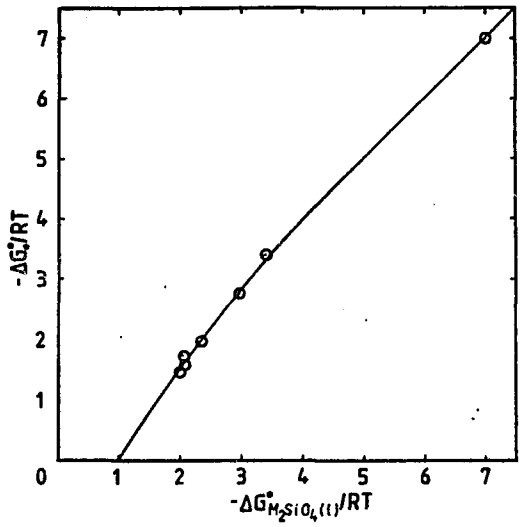

Fig. 16. Calculation of the free energy of formation of depolymerzied basic oxide subsilicate from the free energy of formation of "pure" liquid subsilicate. Figure 11 from the work of Hollitt (1984b).

$$\Omega_1 = \frac{(n_{Si} + n_{O^{2-}})!}{n_{Si}!\, n_{O^{2-}}!} \tag{22}$$

In the case of complete bridge "presence" ($X_{MO} = 0$),

$$\Omega_2 = \left[\frac{\left[\frac{2n_{Si}^2}{n_{Si} + n_{O^{2-}}}\right]!}{\left[\frac{2n_{Si}^2}{n_{Si} + n_{O^{2-}}} - n_{O^o}\right]!\, n_{O^o}!} \right] \tag{23}$$

In "real" systems with incomplete bridge breakage, ΔS^M_C is a function of Ω_1

and Ω_2:

$$\Delta S_C^M = k \ln(\Omega_1 \Omega_2) \quad (24)$$

Hollitt (1984a) applied Sterling's approximation to this and developed

$$\frac{\Delta S_C^M}{R} = A \ln A - n_{Si}^t \ln n_{Si}^t - n_{O}2- - \ln n_{O}2- + D \ln D - E \ln E - n_{OO} \ln n_{OO}, \quad (25)$$

where

$$A = n_{Si}^t + n_{O}2-, \quad (26)$$

$$D = n_{OO} + \frac{n_{O}^-}{2}, \text{ and} \quad (27)$$

$$E = \frac{n_{O}^-}{2} \quad (28)$$

Combining these various components, Hollitt (1984a) developed a formalism for expressing the total free energy of mixing in slags:

$$\frac{\Delta G_M}{RT} = n_{O}^- \frac{\Delta G_O^o}{RT} + n_{\underline{O}} B - \frac{\Delta S_C^M}{R}, \quad (29)$$

This can be related to a_{PbO}, and thus to p_{O_2}, because of the definition of chemical potential, which states:

$$\ln a_{PbO} = \left[\frac{\partial\left[\frac{\Delta G_M}{RT}\right]}{\partial n_{PbO}}\right] \qquad (30)$$

All that is needed now is to do the partial derivation indicated to yield a formula allowing for prediction of p_{O_2} from the various slag parameters.

5.2.3 The Completed Model

It is in fact the accomplishment of this derivation by Hollitt (1984a) that explains why the model under discussion in named after him. The derived formula is:

$$\ln a_{PbO} = \left[\frac{\partial n_{O^-}}{\partial n_{PbO}}\right]\left[\frac{\Delta G^o_{PbO}}{2RT}\right] + B\left[\frac{\partial n_O}{\partial n_{PbO}}\right] - \frac{1}{R}\left[\frac{\partial(\Delta S^M_C)}{\partial n_{PbO}}\right]$$
$$+ \left[\alpha n_{FeO}\,\frac{n^t_{Si} + n_{O^{2-}} - n_{OPb^{2-}}}{(n^t_{Si} + n_{O^{2-}})^2}\right]\left[\frac{\partial n_{O^{2-}}}{\partial n_{PbO}}\right] \qquad (31)$$

Having presented this quagmire, some explanatory material is needed. Firstly, it should be noted that the partial derivatives in Eq. 31 are with respect to constant composition (excepting PbO), pressure and temperature. Secondly, the reader has undoubtedly noticed an "α" not seen before; this is a constant describing the regular-solution interactions between the oxide ions from two basic oxides. Hollitt was forced to determine this quantity empirically, thus revealing perhaps the first weakness of his model.

The distortion energy B is also empirically determined; it is a linear function of 1/T, and is equal to .39 at 1200°C. The final new term in Eq. 31 is $n_{O_{Pb}}{}^{2-}$; this represents the number of moles of oxide ions derived from the "addition" of PbO to the slag. However, it should be remembered that in the slags from this work, the relatively low ratio of basic oxides to silica means that Eq. 15 applies, and that the last term in Eq. 31 can be eliminated.

There are several partial derivatives in Eq. 31, and it is necessary to quantify these expressions before Hollitt's model can be used. First of these is the entropy term:

$$\frac{\partial(\Delta S^{M}_{C})}{\partial n_{PbO}} = -R\left[\frac{\partial n_{O^{o}}}{\partial n_{PbO}} \ln \frac{2n_{O^{o}}}{n_{O^{-}}} + \frac{\partial n_{O^{2-}}}{\partial n_{PbO}} \ln\left[\frac{n_{O^{2-}}}{n^{t}_{Si}} + n_{O^{2-}}\right] + \ln\left[\frac{n_{PbO}}{\sum_{M} n_{M^{2+}}}\right]\right] \quad (32)$$

Again, note the partial derivatives; values for these were specified for the slags equilibrated in this work by Eqs. 13-15. The other partial derivative in Eq. 31 is quantified by:

$$\frac{\partial n_{O}}{\partial n_{PbO}} = \frac{3}{2} \frac{\left[(2\, n^{t}_{Si} - n_{O^{-}})(n^{t}_{Si} + n_{O^{2-}}) \frac{\partial n_{O^{-}}}{\partial n_{PbO}} - n_{O^{-}}\left[2\, n^{t}_{Si} - \frac{n_{O^{-}}}{2}\right] \frac{\partial n_{O^{2-}}}{\partial n_{PbO}}\right]}{C\,(n^{t}_{Si} + n_{O^{2-}})^{2}} \quad (33)$$

In this equation, C is equal to e^{B}, as per Eq. 17. Although this may seem like a considerable mess, what Hollitt has done is to make a_{PbO} calculable from easily obtainable slag chemistry parameters. Applying the partial derivative

values from Eqs. 13-15, we can (thankfully) simplify Eqs. 31-33 to:

$$\ln a_{PbO} = \frac{\Delta G^{o}_{PbO}}{RT} + B\left[\frac{\partial n_{O}}{\partial n_{PbO}}\right] - \frac{1}{R}\left[\frac{\partial(\Delta S^{M}_{C})}{\partial n_{PbO}}\right] \qquad (34)$$

$$\frac{\partial n_{O}}{\partial n_{PbO}} = \frac{3}{2}\left[\frac{2\,(2\,n^{t}_{Si} - n_{O^{-}})\,n^{t}_{Si} + n_{O^{2-}}}{C\,(n^{t}_{Si} + n_{O^{2-}})^{2}}\right] \qquad (35)$$

$$\frac{\partial(\Delta S^{M}_{C})}{\partial n_{PbO}} = R\left[\ln\left[\frac{n_{PbO}}{\sum_{M} n_{M^{2+}}}\right] - \ln\left[\frac{2n_{O^{o}}}{n_{O^{-}}}\right]\right] \qquad (36)$$

Hollitt (1984a) applied this model to three slags: an "industrial" type with no trivalent oxide content, a direct-smelting type with a ferric/ferrous iron ratio of 2.0, and an iron silicate melt with no CaO and a high PbO presence. His calculated PbO activities for the first two slags compared very well with experimentally-determined values, but that of the last mixture was considerably lower than the actual value. The availability of data from this study and from that of Vaskevich et al. (1983) affords an excellent opportunity to further test Hollitt's model against slags with a variety of compositions.

5.2.4 Comparison and Contrast

Table 14 shows data calculated through the use of Eqs. 34-36, with data from the slags equilibrated in this study. The log p_{O_2} values are, as can

Table 14

Calculated Hollitt-Model Parameters, Experimental Slags

(Pb Unit Activity Slags Above Dotted Line; Pb-Ag Alloy Slags Below)

Slag	$\partial n_{\underline{O}}/\partial n_{PbO}$	$\partial(\Delta S_C^M)/\partial n_{PbO}$	log p_{O_2}
1	1.010	41.814	-11.1824
2	.708	43.246	-11.4342
3	.750	38.997	-10.9763
4	.811	45.458	-11.6304
5	.751	34.964	-10.5547
6	.832	37.616	-10.8041
7	.934	38.818	-10.8952
8	.705	40.037	-11.1000
9	.850	33.709	-10.3899
10	.729	26.233	-9.6499
11	.864	33.863	-10.4013
12	.887	30.930	-10.0871
13	.696	41.827	-11.2901
14	.845	33.968	-10.4187
15	.850	29.912	-9.9931
16	.768	30.289	-10.0605
17	.698	26.143	-9.6509
18	.675	24.555	-9.4928
19	1.031	41.133	-11.1042
20	.755	28.566	-9.8851
21	.951	21.586	-9.0893
22	.746	38.568	-10.9329
23	.657	33.388	-10.4219
24	.671	30.638	-10.1298
25	.658	25.735	-9.6218
1	.954	44.819	-11.5153
2	1.093	47.813	-11.7809
3	.950	42.693	-11.2946
4	.840	41.099	-11.1655
5	.957	39.673	-10.9767
8	.751	39.753	-11.0547
9	1.111	37.111	-10.6568
10	.914	38.074	-10.8242
11	.855	34.196	-10.4390
12	.693	32.540	-10.3208
13	.873	29.207	-9.9119
14	1.044	39.988	-10.9801
15	1.103	34.795	-10.4176
16	.931	33.166	-10.3057
17	.707	31.162	-10.1723
18	.910	37.013	-10.7147

be seen, lower than the point where Matyas (1975) claimed that neutral Pb became the only form of lead in solution. These are plotted against the p_{O_2} values predicted by Eq. 9 in Fig. 17, and the reader will note that Hollitt-

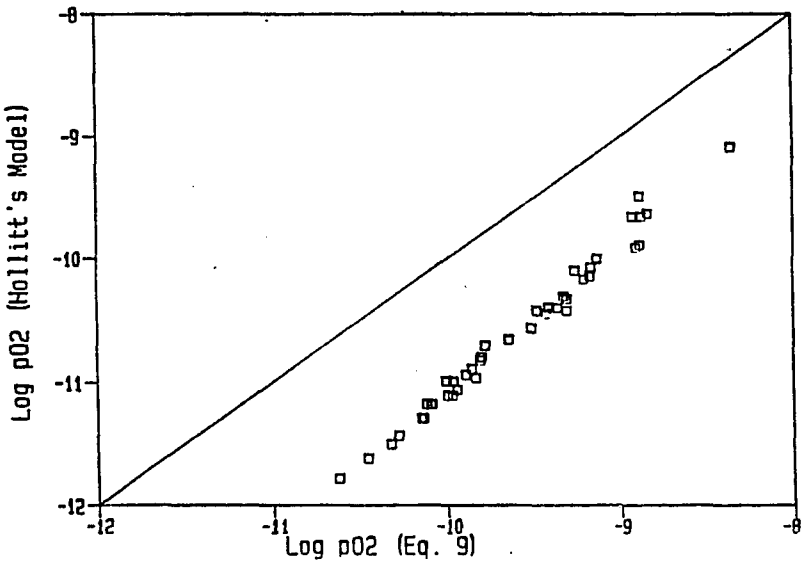

Fig. 17. O_2 partial pressures of experimental slags calculated with Eq. 9 vs. values calculated with Hollitt's model (Eq. 34).

predicted values seem unusually low. The application of Hollitt's model to the data of Vaskevich et al. (1983) can be seen plotted against experimentally-determined oxygen pressures from this study in Fig. 18; again, the anomaly is notable.

In searching for the cause of these discrepancies, attention can be given almost immediately to several of the assumptions used in Hollitt's model. Foremost among these is the assertion that FeO remains coordinated by O^{2-}, even in highly acidic slags. Hollitt himself has stated that this is not the case in all circumstances (Hollitt et al., 1984a); and while other slag

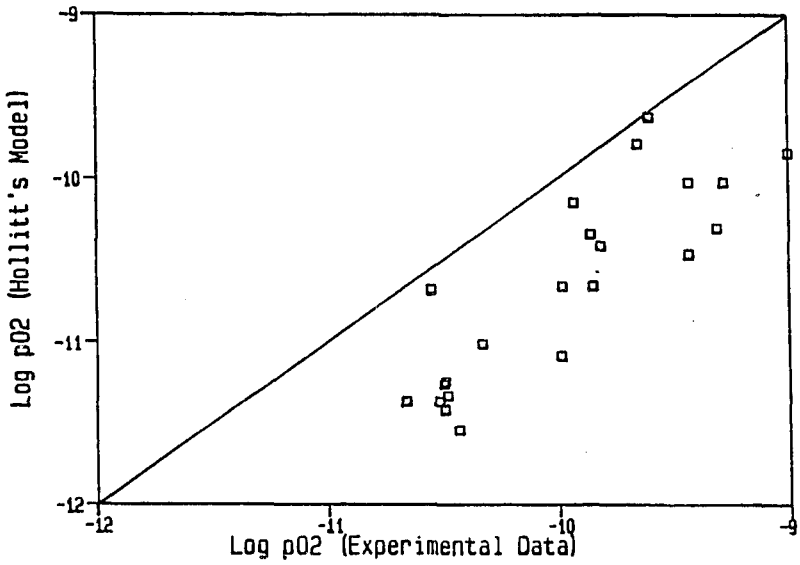

Fig. 18. O_2 partial pressures of the slags equilibrated at 1250°C by Vaskevich et al. (1983); experimentally-determined values vs. values calculated with Hollitt's model (Eq. 34).

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thermodynamicists would agree that FeO is among the least effective of the divalent oxides in bridge-breaking (Lin and Pelton, 1979; Masson, 1972), the conclusion reached by Hollitt in this matter seems an overstatement of his case. Another assumption made by Hollitt with a higher likelihood of validity is that of acidic behavior of amphoteric oxides. It seems logical to state that all of the FeO would engage in bridge-breaking before any $FeO_{1.5}$ or $AlO_{1.5}$ would do so, and if Hollitt's assumption about FeO is even partially correct, such acidic behavior would be a reasonable scenario.

An "adjustment" of Hollitt's model can be made by assuming silicate instead of O^{2-} coordination of all or part of the FeO in the system. If all the FeO is so treated, we can rewrite Eqs. 18-20 as:

$$n_{O^{2-}} = 0 \tag{37}$$

$$n_{O^{-}} = 2\, n_{PbO} + n_{CaO} + n_{FeO} \tag{38}$$

$$n_{O^{o}} = n_{PbO} + 2\, n_{SiO_2} + n_{CaO} + n_{FeO} - n_{O^{-}} \tag{39}$$

These new values can be used to recalculate log p_{O_2} for the slags equili-

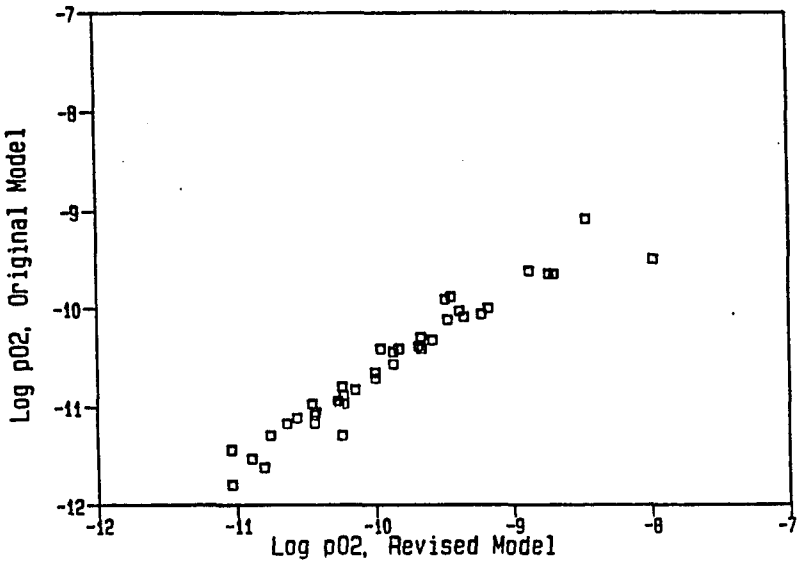

Fig. 19. Log p_{O_2} values derived with "revised" Hollitt model, vs. values from original equations.

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brated in this experiment; the "new" values are shown plotted against the originally-derived values in Fig. 19, and against those calculated with Eq. 9 in Fig. 20. The reader will immediately note a much closer relationship, suggesting that Hollitt's conclusions about FeO coordination in slags are not

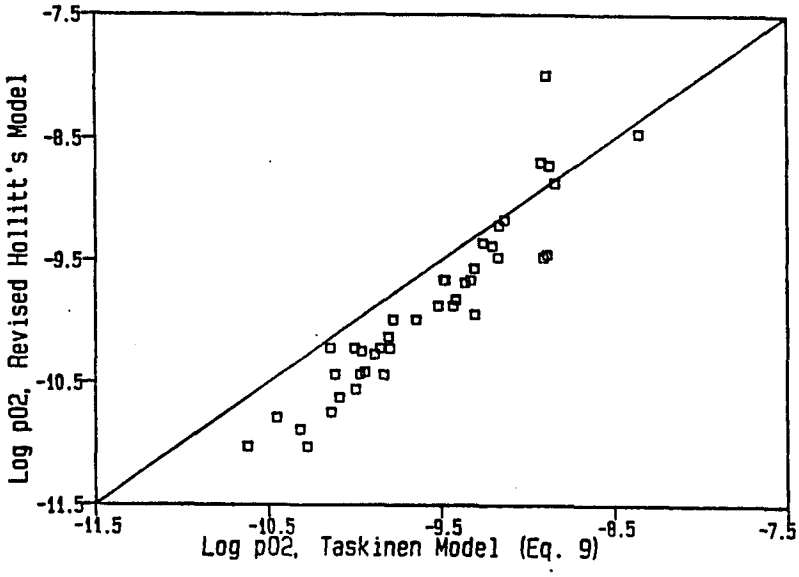

Fig. 20. Log p_{O_2} values derived with "revised" Hollitt model, vs. values calculated with Eq. 9.

valid in this particular situation.

5.3 A Few Words About Zirconia

The use of ZrO_2 as the material of choice for the crucible in which the slags of this work were equilibrated was discussed at some length in Chapter Two. It was pointed out that zirconia represented a compromise of sorts between cost effectiveness and its "excludability" from the system being studied. However, this is based on a rather skimpy research record, and it was felt that this study might be able to shed some additional light on the matter.

Zirconia is a tetravalent oxide, and as was suggested earlier in this chapter, is considered to be acidic in behavior (Gilchrist, 1977, pp. 305-6).

It has found increasing use in recent years as a steelmaking refractory, and this spurred some research effort into its presence in molten oxide systems, most notably at the Japanese refractory maker Toshiba Ceramics (e. g., Oki et al., 1984). Its use as a solid electrolyte has also sparked interest (Theriault et al., 1984), as has its potential in welding fluxes (Bender, 1980).

The work of Kuxmann and Fischer (1974) has already been mentioned as the justification given by Taskinen et al. (1984) for the claim that ZrO_2 content in their slags did not significantly affect the PbO activity. This deduction was made by noting in Kuxmann and Fischer's work that zirconia additions had very little effect on liquidus temperatures in the lead-oxygen binary phase system, which seems a somewhat tenuous element of support. However, similar evidence is available in the work of Bender (1980), working with the $MnO-SiO_2$ binary. Bender found that ZrO_2 additions up to mole fractions of .1 resulted in only insignificant changes in a_{MnO}; since MnO's basicity is roughly equivalent to PbO's (see evidence in Rosenqvist, 1974, p. 328, Lin and Pelton, 1979, and Masson, 1972), it is reasonable to surmise that the results might be equivalent for ZrO_2 additions to the lead silicate system. Other than this, the research record on zirconia's behavior in molten slags is largely nonexistent.

Two matters complicate the analysis of zirconia interaction with the slags equilibrated in this study. The first of these is the "percent zirconia" listed in Tables 6 and 10, which as earlier noted were obtained by subtraction of everything else from 100 percent. It was also mentioned earlier that SEM/EDX analysis of the residue from the sample digestion procedure shows CaO content as well as ZrO_2, so an inherently inaccurate analytical result

can now be seen as even more so. Secondly, the reader will remember that the crucibles used in these experiments were not pure ZrO_2, but rather calcia-stabilized zirconia, with about 5% CaO content. Since CaO would be more likely attacked by an acidic slag and ZrO_2 by a basic one, the relationship between slag analysis and zirconia content would likely be vague at best.

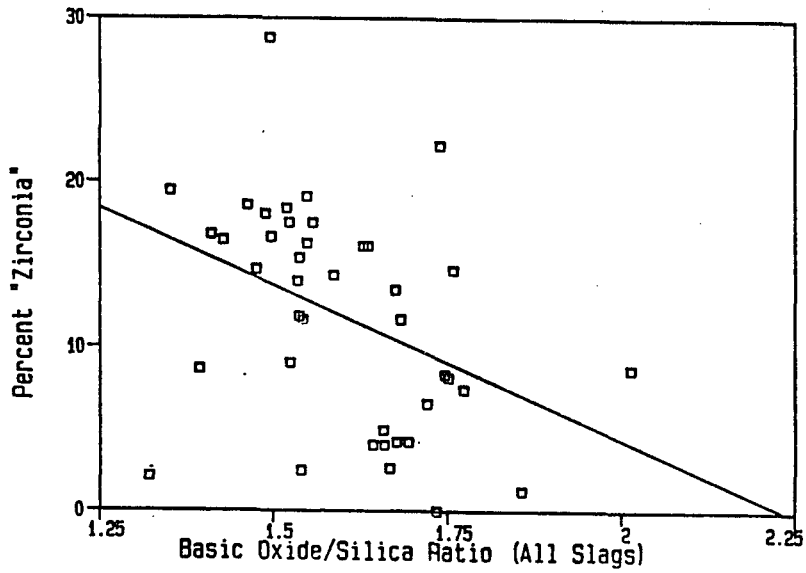

Fig. 21. Empirically-determined slag "zirconia" values vs. basic oxide/silica ratio, experimental slags.

Figure 21 demonstrates this point with a vengeance. Although a least-squares fit of the relationship between percent ZrO_2 and the total MO/SiO_2 ratio shows a negative trend, it is obvious that the correlation is very low. Figure 22, showing a similar relationship with the activity of PbO in the slags (as calculated with Hollitt's model), again demonstrates a slightly negative trend and poor correlation. On the surface, Fig. 22 would seem to disagree

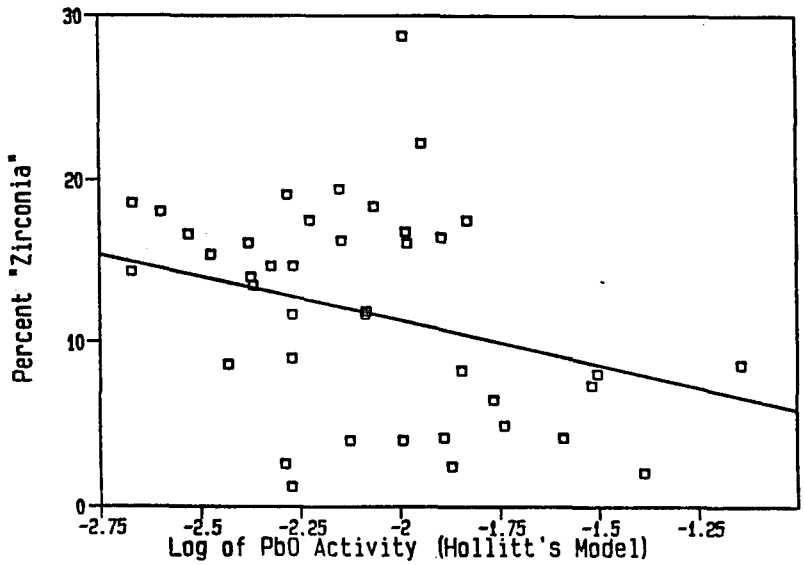

Fig. 22. Experimental slag zirconia contents vs. calculated PbO activity values (Hollitt's model).

with the conclusion reached by Theriault et al. (1984), who correlated higher a_{PbO} values with greater penetration into CaO-stabilized ZrO_2; however, it should be noted that crucible penetration and dissolved zirconia content in the penetrating slag are not necessarily equivalent. It should also be noted that the slag that Theriault et al. used was changed from a PbO/SiO_2 of 1.5 to one of more than 2.0 to demonstrate the effect; as much of the discussion in this chapter would point out, such a change also affects the nature of the slag oxyanions. Nevertheless, the difference points out the need for further study. Figure 22 is also somewhat at odds with the work of Oki et al. (1984), although drawing a conclusion from the two published data points in this study also has risks.

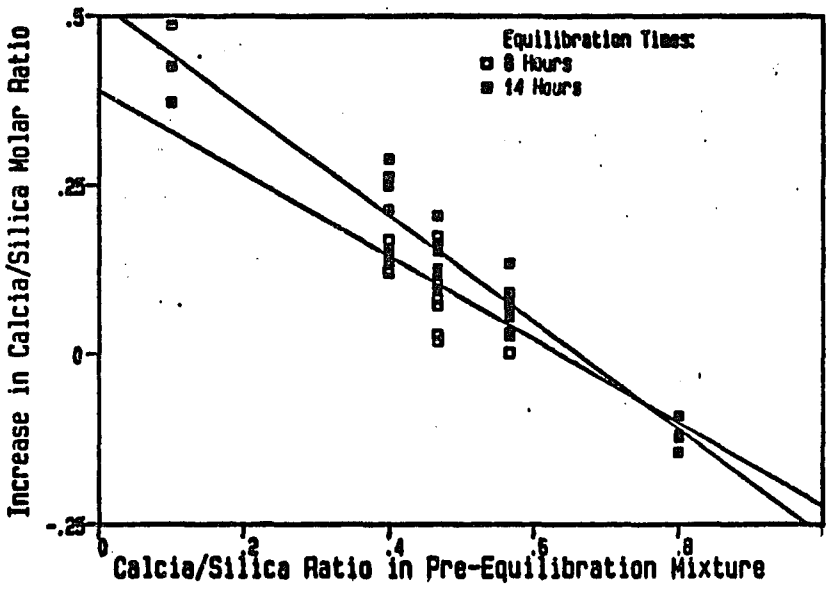

Fig. 23. Increase in CaO/SiO_2 ratio vs. ratio in pre-equilibration reagent mix.

Figure 23 points out a relationship with somewhat greater correlation, namely the "acquisition" of CaO from the crucibles by the equilibrating slags. The conclusion that can be drawn from Fig. 23 is that all the oxide mixtures tended to move (as might be expected) toward a CaO saturation level, and actually "salted out" calcia when too much was added in the initial mix. It seems reasonable to suggest that the leaching of CaO from the crucible wall might make more ZrO_2 surface available for reaction with the slag, and thereby lead to higher zirconia contents in acid slags. Zirconia's acidic properties counterbalance this characteristic, of course, and the time limits of the experiments make the drawing of firm conclusions largely impossible. In a sense, the difference between the "daytime" (8 hr.) and "nighttime" (14 hr.) equilibration times dramatized in Fig. 23 point out that the experimental

slags were never in a better-than 'quasi' equilibrium, and that only the use of a truly system-neutral crucible material (such as iridium) would have made a difference in this matter.

CHAPTER 6

CONCLUSIONS

6.1 Experimental Procedures

In general, it can be stated that the experimental and analytical procedures used in this study produced satisfactory results. However, a more thorough examination will perhaps better point out the strengths and weaknesses of the regime, as well as areas where further experimental work might yield improvements.

The sealed-ampule method discussed in Chapter Two was one of the procedural steps that yielded the most positive results. Its successful employment does require some training in glass-working techniques, and not even the considerable experience developed by the author in sealing 43 ampules prevented a certain amount of glass breakage. It should also be noted that fused silica tubing becomes unusuable at temperatures somewhat higher than the 1200°C used in this study. Nevertheless, this choice of ampule-sealing method is to be recommended where usable.

The choice of crucible material has been extensively discussed in Chapter Two and Five, and the weaknesses inherent in its use are no secret. In fact, the thermodynamic effects of zirconia in molten oxide mixtures are an extremely fertile field for future research, and it is hoped that the results of such research will someday be available. One research tactic that would be helpful in this regard would be the use of larger crucibles and amounts of

slag mixture; this would result in a decrease in the amount of crucible surface area relative to slag weight, making ZrO_2 solubility less apparent.

The concern over using calcia-stabilized zirconia crucibles, illustrated in Fig. 23, points out one weakness in the experimental procedure, namely the inconsistency of equilibration times. While there is little evidence to suggest that the differences in these times caused any inconsistency in the relationship between lead oxide solubility and other slag parameters, the variance in CaO pickup from the crucible is in itself a cause of concern, which could be eliminated by constant equilibration times. The use of large crucible and samples suggested above would of course require even longer run times than those used here.

The use of silver as the alloy metal for reducing a_{Pb} also proved satisfactory, both in terms of procedure and results. Several of the graphs in Chapter Five demonstrate that the "corrected" PbO levels in the alloy slags display indistinguishable relationships to other slag parameters from those equilibrated in contact with pure Pb. However, the goal stated in Chapter Two of using Pb-Ag alloys to produce slags with low lead content seems to have been negligated by the more-than-low-enough results achieved with the "a_{Pb}= 1" slags, making the question somewhat moot. A future research project of some value in this area would be the determination of the thermodynamic properties of Pb-Au alloys at 1200°C; gold is even less soluble in slag than silver (Meyer and Richardson, 1957), and thus a better choice for this role.

The analytical procedures used in this study can also be considered satisfactory, but in some need of improvement. Specifically, a means of get-

ting ZrO_2 into a digestion solution along with the other slag constituents would make for much more meaningful results than those fruitlessly analyzed in the last section of Chapter Five. Another analytical technique whose development would be of interest is a spectrophotometric technique for lead analysis, which would likely have much better accuracy than the atomic absorption method employed in this work. PAR-4 (2,4-pyridylazo resorcinol) is a possible reagent.

6.2 Results

Regardless of the model used, it has been conclusively shown that PbO solubility in slags is a direct and linear function of the partial oxygen pressure at low (less than $10^{-8.5}$) p_{O_2} values. There is some degree of support for the conclusion reached by Taskinen et al. (1984) that such is not the case at higher oxygen pressures. The results of this study also agree with that of Taskinen et al. in showing that the relationship between PbO content and ferric/ferrous iron content is not as direct, especially at lower lead levels. It should however be noted that both of the models used for calculation of p_{O_2} show that this value is a function of various slag parameters, and that changing these parameters (CaO/SiO_2 or Fe/SiO_2) can affect the PbO solubility by changing p_{O_2}. The effect is more direct at higher lead levels.

The first of the models used for the calculation of p_{O_2} was adapted from the data compiled by Taskinen et al. (1984), and featured the use of a curve-fitting exercise to express the activity coefficient of lead oxide as a function of the slag chemistry. This expression was then fitted into the thermodynamic relationship between a metallic lead phase and slag-dissolved

PbO to yield a completed formula for the solubility of the latter. This method suffers from the drawbacks of 1) having to extrapolate outside of the p_{O_2} ranges used in the Finnish study, 2) lack of provision for slag constituents other than PbO, SiO_2, FeO_x and CaO, and 3) the empirical nature of the activity coefficient relationship. However, it appears to be a useful tool for prediction in a relatively simple system.

The other model used was developed by Hollitt (1984a,b) from the "broken-bridge" theory as discussed by Lin and Pelton (1979). This model uses the effects on the molecular structure of a molten silicate melt of the addition of a basic oxide to calculate the free energy of mixing caused by that addition, and thus the activity of the basic oxide (which allow calculation of p_{O_2}). Hollitt's model remedies many of the drawbacks which affect the Taskinen curve-fit, but has defects of its own. These include 1) the use of questionable assumptions regarding the behavior of FeO (and possibly other oxides less basic than PbO), 2) the lack of an adequate description for the effects on slag structure of the amphoteric oxides present in a slag, and 3) the need for an empirical term to complete the characterization of the relationship between basic oxide molecules. However, Hollitt's model has more applicability to "real" slags than that developed in this study, and this recommends its further development.

APPENDIX A

PROGRAM FOR CALCULATING CRUCIBLE CHARGE WEIGHTS

```
C     THIS PROGRAM USES INPUT CALCIA/SILICA RATIOS AND ESTI-
C     MATED FINAL FERRIC/TOTAL IRON RATIOS TO CALCULATE THE
C     WEIGHT OF VARIOUS LAB REAGENTS (IN THIS CASE, CaO, SiO2,
C     'FeO', Fe2O3 AND PbO) TO A SMALL ZIRCONIA CRUCIBLE
C     FOR SLAG EQUILIBRATION IN CONTACT WITH MOLTEN LEAD OR
C     A LEAD ALLOY.
C     X'S ARE MOLECULAR WEIGHTS; Z'S ARE RATIOS OF ELEMENT
C     WEIGHTS (Pb, Ca, Fe, Si) TO THAT OF OXIDE.  SLAGWT IS
C     THE WEIGHT OF SLAG THAT WILL FIT IN THE CRUCIBLE; IT
C     SHOULD BE LOWERED FOR HIGHER CALCIA/SILICA RATIOS.
C     FESI IS THE TOTAL IRON/SILICA RATIO, AND CAN ALSO BE
C     CHANGED.
      N=0
      XSIO2=60.08
      XCAO=56.08
      XFE2O3=159.69
      XFEO=71.85
      XCAOH2=74.09
      ZSIO2=28.064/XSIO2
      ZCAO=40.08/XCAO
      ZFE2O3=(2.*55.847)/XFE2O3
      ZFEO=55.847/XFEO
      SLAGWT=.7
   10 WRITE(5,*) 'Please enter CaO/SiO2 and ferric/total iron ratios,'
      WRITE(5,*) 'and enter weight percent lead oxide.'
      READ(6,*) CASI, FER, WTPBO
C     THE FOLLOWING STATEMENT CAN BE USED WITH A LEAD ALLOY
C     TO EXPRESS THE EFFECT OF REDUCED Pb ACTIVITY.  IN THIS
C     CASE, a_Pb = .25.
```

```
      WTPBO=WTPBO/4.
      N=N+1
      YCAO=CASI
      WTCAO=YCAO*XCAO
      YFE=FESI
      YFE2O3=(YFE*FER)/2.
      YFEO=YFE-YFE*FER
      WTSIO2=XSIO2
      WTFE2O3=YFE2O3*XFE2O3
      WTFEO=YFEO*XFEO
      WTPBO=(WTPBO/100.)*SLAGWT
      WTTOTAL=WTCAO+WTFEO+WTFE2O3+WTSIO2
      WTLEFT=SLAGWT-WTPBO
      WTRATIO=WTLEFT/WTTOTAL
      WTCAO=WTCAO*WTRATIO
      WTFEO=WTFEO*WTRATIO
      WTFE2O3=WTFE2O3*WTRATIO
      WTSIO2=WTSIO2*WTRATIO
C     FOR ANALYTICAL PURPOSES, IT WOULD BE USEFUL TO KNOW
C     THE PERCENTAGES OF THE VARIOUS ELEMENTS IN THE FINAL
C     MIXTURE.  THE THREE FOLLOWING STEPS ARE FOR THAT
C     PURPOSE.
      CCA=(100.*ZCAO*WTCAO)/SLAGWT
      CSI=(100.*ZSIO2*WTSIO2)/SLAGWT
      CFE=100.*(ZFEO*WTFEO+ZFE2O3*WTFE2O3)/SLAGWT
      WRITE(22,*) 'For trial', N, 'try adding:'
      WRITE(22,20) WTFEO, 'grams of FeO,'
      WRITE(22,20) WTCAO, 'grams of CaO,'
      WRITE(22,20) WTFE2O3, 'grams of Fe2O3,'
      WRITE(22,20) WTPBO, 'grams of PbO, and'
      WRITE(22,20) WTSIO2, 'grams of SiO2.'
      WRITE(22,*) 'This slag will have'
      WRITE(22,40) CCA, 'percent Ca,'
      WRITE(22,30) CFE, 'percent Fe, and'
      WRITE(22,30) CSI, 'percent Si.'
   20 FORMAT (F7.3, A20)
   30 FORMAT (F5.2, A16)
   40 FORMAT (F5.2, A12)
      WRITE(5,*) 'Please sir, may I have some more?'
      WRITE(5,*) '(0=Yes, 1=No)'
      READ(6,*) I
      IF (I.EQ.0.) GOTO 10
      END
```

APPENDIX B

PROCEDURE FOR FERROUS/TOTAL IRON ANALYSIS

Note: this procedure assumes the use of ordinary-grade (i. e. cheap) bottled nitrogen gas, purified by passing through copper turnings in a tube furnace heated to 1200° F.

1. Before starting, make sure that pinchcocks are in first position (see Fig. 5), nitrogen control stopcock is closed (this forces the N_2 through the digestion vessel), buret stopcock is closed, all other valves are open, and all stoppers are closed.

2. Open up N_2 cylinder, and establish slight flow of gas using the bubbler for reference. Turn on furnace, set to 1200° F. It will take approximately two hours for the furnace to warm up.

3. As the furnace gets close to temperature, weigh out about 30-50 milligrams of slag. Quickly raise the buret off the top of the digestion vessel, and using the weighing paper as a funnel, empty the sample into it. Replace the buret and turn up the nitrogen for a few minutes to purge the vessel of any air that might have entered during the sample introduction.

4. After a few minutes, measure out three to four milliliters of concentrated HCl (36%). Empty into buret, and slowly drop into digestion vessel. Close stopcock just before buret empties; this prevents air access to vessel.

5. After a few minutes, turn down nitrogen flow (to save gas). Then go away and do something else. A watched sample never digests, and an unwatched one needs at least four hours.

6. Measure out 10 ml. of distilled water, and add to digestion vessel in the same manner as the HCl. Light a Bunsen burner, and heat solution until first signs of boiling are noticed; shut off burner. (This will hopefully cause the digestion of any small particles of slag knocked out of the solution by falling drops of HCl.)

7. Weight out two grams of hydroquinone into a 50-ml. Erlenmayer flask, and fill to mark with distilled H_2O. Add magnetic stir bar and dissolve hydroquinone; no heat is required. When dissolution is complete, measure out 50 ml. of this solution into an appropriately-sized graduated cylinder (accuracy in the amount of solution added is more important than accuracy in the amount of hydroquinone used), and add to the total iron flask. Doing this at this time gives the flask a chance to purge before solution is added.

8. Weigh out .3 gm. of 1,10-phenanthroline monohydrate into a 100-ml. beaker or Erlenmayer flask, and fill to about 10 ml. above mark with distilled water. Add stir bar and dissolve as before, with the exception that the mixture must be heated to near boiling before this will occur (thus the extra liquid). Even then, it takes some time, and you need not stand over it and watch while the stuff dissolves.

9. Open up N_2 control stopcock and make sure that the solution distribution nozzle has been raised above the 1000-ml. mark.

10. Fill the buret with distilled water, and empty it into digestion vessel, again being careful to always leave some liquid in the bottom of the buret. Repeat until vessel is full, i. e. the gas inlet or outlet is all but closed off by the liquid level.

11. Close diluted solution stopcock and pump contents of digestion vessel into diluted solution vessel. (A few seconds should be allowed to let stirred-up undigested slag material settle to the bottom of the digestion vessel.) The lines need not be pumped entirely dry. When no more liquid is being drawn from the bottom of the digestion vessel, return to step 10. Repeat until diluted solution vessel is filled to the mark.

12. Move pinchcocks from first position to second position (see Fig. 5). Lower solution distribution nozzle to approximately the bottom of the diluted solution vessel, and make sure the solution distribution stopcock is open to one of the two iron flasks. Turn up the nitrogen a good deal, to prevent backflow through the bubbler during the second-stage pumping.

13. Pump solution from the diluted solution vessel into the two iron flasks, making sure to switch flasks using the solution distribution stopcock every so often to ensure homogeneity in the two splits. Four hundred milliliters are to be pumped into each; remember that there is already 50 ml. of hydroquinone solution in the total iron flask. When done, shut the pump off.

14. Remove stopper assemblies from both iron flasks, and cover immediately with "uninjured" rubber stoppers. Set the flasks aside, remembering which one is which.

15. Pump remaining solution in diluted solution vessel into a beaker of some sort until lines are dry. While pumping, remove digestion vessel from apparatus, and thoroughly clean out. When pumping is done, shut pump off, and do likewise to diluted solution vessel. It will not need to be dried thoroughly, but the digestion vessel will. Turn down N_2 flow, to save gas supply.

16. The hydroquinone in the total iron solution will need about 30 minutes to do its job. When this time elapses, measure out 50 ml. of the now-cooled phenanthroline solution into each flask (again, quantity of liquid is of more concern than quantity of reagent). Complexing will take another 30 minutes. While waiting, the spectrophotometer can be warmed up and standardized against a cuvet containing distilled water.

17. While waiting, it will also be necessary to dilute the solutions. A 2:1 dilution with distilled water will ensure that the iron content of the liquid is within the linear range for iron concentration (< 5.0 ppm).

18. In taking readings, several items are worth noting:

    1) As mentioned in the text, polystyrene disposable cuvets tend to promote reduction of ferric iron in solution to ferrous; prudent use of these is urged.

    2) In doing calculations, the effect of diluting solutions - the hydroquinone and phenanthroline, and the 2:1 H_2O split - should not be neglected. The potential for math mistakes is substantial.

    3) Solution concentrations should be measured against a complexed 5.0 ppm Fe standard, which can be made from ferrous ammonium sulfate hexahydrate (.0371 gm./liter) dissolved in water and complexed with phenanthroline solution as above. Spectrophotometer readings can change from day to day, so the standard spectrophotometer reading should **not** be assumed as a constant.

    4) Two sets of readings should be taken, approximately twenty minutes apart (in new cuvets). This will ensure that complexation is complete.

19. During the various waits involved in the reading-taking process, the digestion and diluted solution vessels can be put back in place, the solution distribution nozzle raised, the N_2 control stopcock closed, the diluted solution stopcock opened, the pinchcocks returned to their original positions, and all other matters necessary to restart the process undertaken. It is also a timesaver to weigh out the next sample and put it in the bottom of the digestion vessel (assuming the latter is dry). The buret should have been completely emptied while the digestion vessel was "out to dry."

20. When readings are complete, empty all flasks and wash out with distilled water - again, complete drying isn't necessary. Replace into apparatus and use the bubbler to stabilize nitrogen flow. Go to steps 3-4 and redo as often as liked.

APPENDIX C

CALCULATIONS FROM OTHER WORKS

The reader will recall that in Chapter Five use of was made of data and figures from the work of Taskinen et al. (1984) to derive various mathematical functions, and for comparison with data from this study. In addition, the similarity in type of research between that work and this one has been repeatedly brought across. Therefore, a fuller discussion of that paper and its use in connection with the data from this research is in order.

The actual paper published by Taskinen et al. did not actually contain any written data; points have instead been derived from the graphs, several

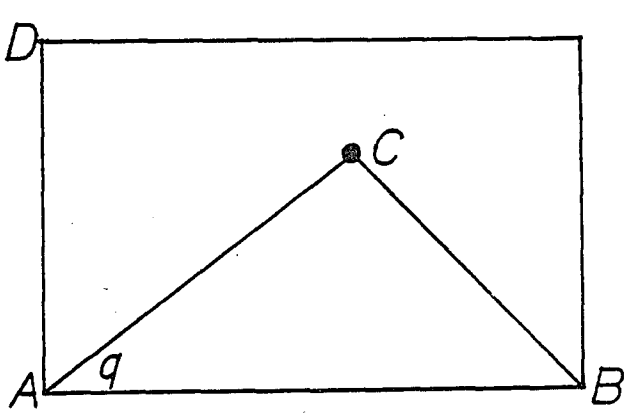

Fig. 24. "Triangulation" method of data interpolation.

of which are reproduced in this work. Figure 24 shows how numbers were

created from these graphs. The method shown is a 'triangulation' method of sorts, using points A and B, corners of the graph area. (It should be noted that the graphs actually used for this process were xeroxed enlargements of the original, to improve accuracy.) The distances between these points and point C, the data point whose coordinates were sought, were measured with a ruler, as was that between A and B. Knowing the length of the three sides of a triangle allows calculation of the three angles, including in this case angle q at the lower left hand corner. The vertical coordinate of point C is then equal to $\overline{AC}$, the length between points A and C, times sin q; the horizontal coordinate equals $\overline{AC}$ cos q. Comparing these against $\overline{AB}$ and $\overline{AD}$ (the vertical length of the graph area) allows the calculation of the data values represented by point C.

This method works reasonably well, but should be used with some caution. It is not as accurate in areas towards the bottom of the graph, especially at the horizontal center; vertical coordinate values are especially suspect for points calculated from this area. By employing measured distances between two exact points, it does however eliminate the possible error in trying to measure the perpendicular distances between a data point and the graph boundaries.

The reader may have noted that none of the data points displayed by Taskinen et al. are actually related to a log p_{O_2} value; this of course leads to the question of how the relationships involving this variable were derived. The answer lies in the iso-log p_{O_2} lines shown in Figs. 6 and 7, and the iso-CaO/SiO_2 lines which they intersect. These latter lines are of course interpolations between the data points in the figures; whether they represent a

mathematical function or are just freehand-drawn lines is not mentioned in the paper. The intersections between these two types of lines in Figs. 6 and 7 provided the data "points" used for the derivation of the relationships involving log p_{O_2} discussed in Chapter Five. However, the backcalculated values of the O_2 partial pressure used later on were derived with the X_{PbO} values of the actual data points. Actual data points were also used for calculating the relationships involving PbO weight percentages and the ferric/total iron ratio.

It should be admitted here that there are several sources of possible error inherent in this procedure. The method of data point coordinate measurement must certainly be first on this list, despite the belief here that it is inherently the most accurate. The use of "best-fit" iso-CaO/SiO_2 lines for log p_{O_2} calculations is a second possibility. However, some difficulties in the paper itself also merit some concern. Actual analyses of the various slags Taskinen et al. equilibrated were not published, and it seems questionable at best to assume that their CaO/SiO_2 and Fe/SiO_2 ratios were constant to four significant digits. It also must be asked in the treatment of this as well as any other paper how accurately the data points were plotted in the first place; the interpolator can only assume reasonably close agreement. Lastly, little was said about Taskinen et al.'s method of ferric/ferrous iron analysis, and this leaves some uncertainty. However, it is felt that use of the data in its as-published condition was necessary to adequately discuss the results of this study.

APPENDIX D

REVIEW OF LEAD AVAILABILITY IN SLAG LEACHATE

As stated in the Preface, the original reason for undertaking the experimental work described above was concern over the properties of lead blast-furnace slag as a waste material. The hope is that the results will allow for the creation of artificial slags with controllable low-level levels of lead oxide at varying calcia/silica and iron/silica ratios, for use in planned future studies of slag leaching characteristics. A brief review of this latter problem may then be of some use.

The specific concern stems from the definition under the regulations of the Resources Conservation and Recovery Act (RCRA) of what constitutes a hazardous waste. Part of this definition includes the setting of maximum levels of various metals in the leachate solutions from a waste material. For lead, this limit is 5.0 milligrams/liter (ppm); for cadmium, 1.0 ppm. A solution with levels over this would be characterized as toxic, and thus presumably liable to various penalties under the RCRA rules. Pb and Cd are singled out in this discussion because they are the two metals most likely to be available in the leachate from lead blast-furnace slag.

The Environmental Protection Agency (EPA), charged with administering the provisions of RCRA, currently uses a self-designed Toxicant Extraction Procedure (TEP) to test various waste materials for susceptibility to

availability of toxic metal content in leachate from that material (Webster and Perket, 1984). TEP involves leaching a specified amount of material (100 gm.) in a specified amount of leach liquor (1600 ml.) for a specified period of time (24 hr.) at a specified pH (5.0) maintained with a specified acid (acetic). Tests conducted with actual lead blast-furnace slags (Robbins, Bundy and Stanga, 1983) have shown that TEP results are considerably over the limits for Pb and Cd mentioned above.

However, TEP has potential drawbacks which mineral industry spokesmen have been quick to discover (Robbins, Bundy and Stanga, 1983; Webster and Perket, 1984). As Robbins, Bundy and Stanga point out, TEP was developed to simulate conditions in municipal landfills, and "slag is not stored under conditions where it may be subject to organic acids or comingled with materials which have potential for organic acid formation." Thus, the use of acetic acid for maintaining pH is questioned, as is the use of pH 5.0 itself. Other objections include the EPA's specification (or lack thereof) of sample size, age and storage conditions before testing, and test temperature range (Webster and Perket, 1984).

Testing has also been done under what are possibly more reasonable conditions. The use of distilled water as the "leachant," at pH 7.0 produced leachate well within the RCRA limits, especially in regard to lead (Robbins, Bundy and Stanga, 1984). In addition, keeping the pH at 5.0 but using a different acid to maintain it also makes a difference (Webster and Perket, 1984); specifically, inorganic acids such as HCl, HNO_3, and especially H_2SO_4 are associated with a considerable reduction in Pb availability from blast-furnace slags. Although it may be somewhat questionable whether the pre-

cipitation in the vicinity of a blast furnace is actually as high as 7.0, several of the objections seem to have considerable merit, and correcting the testing method is of obvious importance to the lead industry.

A weakness is discussing this controversy lies in the nature of the tests to date, which have been conducted with actual blast furnace slags. The difficulty is that such slags are certainly not comparable in composition between studies done at different places, as may be inferred from the Introduction of this work. Comparison of results is thus rendered more difficult, since it may very well be that differing parameters of the slags' creation and processing could affect leaching results. In addition, most actual slags are multiphase concoctions (Lenz and Lee, 1984), and the relative amount of various phases is also a variable in leaching results. Finally, a point from the Introduction should be resurrected in noting that much of the actual lead in slag is not dissolved Pb or PbO, but rather entrained droplets of bullion. Again, these would certainly respond differently to leaching than lead in solution; being able to quantify the difference would prove most useful.

A new study on lead blast-furnace slag leaching characteristics might then not just focus on variations in test procedure; it might also consider differing parameters in the slag itself. Changing CaO/SiO_2 and Fe/SiO_2 ratios are the first that come to mind, but others, such as replacement of part of the CaO by MgO or FeO by MnO might also have value. The use of a single-phase (glassy) material would also remove one "degree of freedom" from the results, making them more comparable. The results from this study make it possible to change such parameters and still maintain a constant percentage of lead in the slag for more comparable leachate tests. Such an experimental

program would hopefully remove much of the confusion over slag-leaching tests, and make development of a more realistic procedure easier.

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