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A new and direct process for the reduction of lead sulfide

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A NEW AND DIRECT PROCESS FOR THE REDUCTION OF LEAD SULFIDE

BY

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Approved by

A. E. Morris (Advisor) T. J. O'Keefe

ABSTRACT

The direct reduction of lead sulfide concentrates by iron was investigated. An oxygen-bearing flux was shown to be a necessary ingredient for complete reduction of the concentrate. The effects of time and temperature on lead recovery were studied. Only a trace amount of sulfur dioxide is evolved during reduction, which is in agreement with thermochemical calculations.

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I. INTRODUCTION

Commercial lead ores contain galena (PbS) as the principal ore mineral. The extraction of lead from the ore takes place first by a flotation concentration step, in which a relatively pure lead sulfide concentrate is produced. This concentrate is then roasted (sintered) to drive off the SO_2, while almost all of the metal is oxidized. The roasted concentrate (calcine) is then smelted in a blast furnace to reduce the lead oxide to metal. The crude lead produced is then sent to a refinery. The conventional lead smelting process described above has changed little over the past 50 years.

The evolution of sulfur dioxide during the sintering step is a source of air pollution in the vicinity of a lead smelter. Some of this SO_2 may be captured in an acid plant, if the smelter has one, but the very nature of the conventional sintering operation makes it practically impossible to recover more than about 60% of the SO_2 in the acid plant. If lead is to be extracted from sulfide ores without any appreciable emission of SO_2 to the atmosphere, the conventional lead smelter must be modified with extensive SO_2 removal equipment at great cost, or entirely new lead extraction processes must be developed which do not emit SO_2 in the first place.

In the present investigation, the feasibility and practicality of a direct lead smelting process was examined, in terms of time, temperature, and amount of flux and reducing agent added in order to obtain the maximum recovery of lead. In general, the objectives of this investigation were:

1. To demonstrate that the lead in a commercial concentrate can be nearly completely reduced in a single-step direct reduction process,
2. To examine the relationship between time, temperature, relative amounts of fluxing ingredients and reducing agent, and type of fluxing agent, so as to determine the effect of each, and thereby arrive at some nearly optimum set of reducing conditions for maximum lead recovery,

3. To determine the amount of SO_2 evolved during the reduction,
4. To examine the nature and composition of phases formed during the reduction, and
5. To find out enough about the process to conduct the research and development work necessary to make the process attractive on a commercial scale.

Prior to the present investigation, a few brief investigations were carried out by students under the supervision of Dr. A.E. Morris, who has filed a patent disclosure and application on the process.

II. REVIEW OF LITERATURE

A. Introduction

The conventional lead smelting process is a combination of roasting, followed by a blast furnace smelting step. The main environmental problem associated with lead smelting is the emission of sulfur dioxide which above a certain concentration is hazardous to human health and plant life. The Department of Health, Education, and Welfare has discussed the effects of sulfur dioxide on health[1]. Adverse effects were detected when the average SO_2 concentration exceeded 0.11 ppm for three or four days or when the annual average exceeded 0.04 ppm.

B. Present Situation of Lead Smelting

A survey of present lead smelting practices was reviewed by McNaughton[2] in 1968; no significant changes have taken place in the industry since that time. In the year 1971 the State of Missouri[3] produced 404,230 short tons of lead, which was nearly 75% of the total U.S. output. Two of the three smelters in Missouri have sulfuric acid plants, while the other disperses SO_2 through a tall stack. In the same year these smelters released to the atmosphere 62,600 tons of SO_2 assuming a 50% recovery of sulfur as acid.

The U.S. Bureau of Mines has recently published an extensive account of the impact of sulfur dioxide control on the domestic nonferrous smelters[4]. Their most important conclusions: pollution control regulations already implemented or being considered will require a substantial investment of money to reduce emissions of sulfur dioxide. Modifications of the existing lead smelters so as to bring the SO_2 concentrations down to proposed standards will cause an increase in production cost, which will increase the price of metallic lead. However, the pollution problem will not be completely solved even if sulfuric acid plant technology could capture most of the SO_2. The production of sulfuric acid may be greater than that which can be sold or given away. Thus an air pollution problem may be converted to a solid waste problem if excess of sulfuric acid must be neutralized with lime. The concept of 100% emission control will necessitate a careful reevaluation of present processes[5,6].

C. Alternative Processes

The most economic way of meeting future air quality standards will probably be the adoption of a different process for the extraction of lead rather than trying to modify the present one. Such a different process could be a modification of an older process or might be an entirely new process. The following sections will review the known older and newer pyrometallurgical processes that have been suggested for the extraction of lead from its sulfide concentrate. No attempt is made to review hydrometallurgical processes.

1. The Precipitation Process

The use of iron in reducing lead sulfide was common at the end of the last century[7,8,9] and was called the precipitation process. It was carried out in a reverberatory or blast furnace and used coke as fuel and metallic iron as reductant. It was only applicable to rich lead ores containing small quantities of antimony and arsenic. The products formed were metallic lead and a mixture of iron and lead sulfides, the so-called lead matte. When this method was used for ores with a large percentage of silica and silicates, problems arose on account of the high temperature required and the high consumption of metallic iron.

A version of the precipitation process operated in Upper Harz (Germany) up to the end of the last century[10]. A reverberatory or blast furnace was used, and for taller blast furnaces the source of iron was iron oxide which was reduced by the coke. Other sulfides like As, Sb, and Cu took up an additional amount of iron. Zinc sulfide may have been partly decomposed by metallic iron. 20 to 25% of the charge was iron, but the loss of considerable lead in the matte was a real problem in this plant. In the above plant some lime present in the ore together with carbon may have reduced PbS according to the following equation:

$$PbS + CaO + C \rightarrow Pb + CaS + CO \qquad (1)$$

Variations of the precipitation process using metallic iron and lead sulfide or iron ore and carbon, were carried out in a hermetically closed electric furnace[11]. The lead was drawn off in liquid form and lead vapors were condensed from the gaseous products. Prior to 1900 a plant operated in Chicago on high silica argentiferous ores[12] using the precipitation process. Lime, chlorine and fluorspar were used as fluxes but the recovery was only 75%.

2. The Salt Process

Betts[13] found that PbS can be reduced by the action of carbon or carbon compounds, iron oxides and a sodium salt to form sodium sulfide. The reduction takes place according to the reactions:

$$Na_2CO_3 + 2C + PbS \rightarrow Pb + Na_2S + 3CO \qquad (2)$$

$$Fe_2O_3 + 3C + 2PbS \rightarrow 2Pb + 2FeS + 3CO \qquad (3)$$

The smelting is carried out at moderate temperatures in a reverberatory furnace to yield metallic lead and a heavy metal-alkali metal matte. In a later version of the salt process, Pendar[14] patented a method for extracting lead from its sulfide by Na_2CO_3, lime, sodium chloride, carbon, and an oxide selected from the group of Zn, Fe, and Si. The main composition of the matte is Na_2S and FeS. Na_2CO_3 alone was not adequate because of the high melting point of Na_2S, so FeS was produced to lower the melting point. Introduction of sodium chloride in the mixture may produce a chlorination action on the lead. The patent claims a recovery of 96%, but low pressures are needed for the separation of the lead vapor.

3. Aluminum Reduction Process

Mellgren and Coffin[15] recently patented a process to recover metallic lead from its sulfide using a fused salt cover with molten aluminum as reductant. Chesti and Sircar[16] in 1972 investigated a direct smelting method using aluminum according to the following equation:

$$3PbS + 2Al \rightarrow 3Pb + Al_2S_3 \quad (4)$$

The temperature for this process was maintained between 1200° to 1300°C with a maximum yield of 87%. If the concentrate is low in lead content (less than 50%) the recovery is also low. The presence of large amounts of silica and other materials demands more aluminum in the charge which in turn causes a higher cost. This process is clearly a version of the precipitation process except that aluminum is used instead of iron.

4. The Reduction Roasting Process

This process is based mainly in the Self-Fluxing Lead Smelting method described recently by Schwartz and Haase[17]. The PbS is oxidized to PbO and $PbSO_4$, and these compounds react with the undecomposed PbS according to the following equations:

$$PbS + 2PbO \rightarrow 3Pb + SO_2 \quad (5)$$

$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2 \quad (6)$$

Fuller[18] of St. Joe Minerals has recently investigated a single step process in which the lead sulfide is oxidized with lead oxide in solution in molten lead. However excessive refractory attack was a serious problem in this process.

5. Hydrogen Reduction Process

Hydrogen has been shown to act as a reducing agent for different sulfides, especially in the presence of lime[19]. Spagnola[20] obtained 95 to 99% reduction of galena by hydrogen. The reduction started at 440°C, with complete conversion to free lead at 600°C. More rapid decomposition was found at 1000°C. The reaction that takes place is the following:

$$PbS + H_2 \rightarrow Pb + H_2S \quad (7)$$

This process needs large amounts of hydrogen and from 1 to 3 hours for complete reduction of 1/2 gram of fine concentrate.

The U.S. Bureau of Mines is presently conducting research on the hydrogen reduction of vaporized lead sulfide[21].

D. Summary and Conclusions

In all the processes discussed previously the best possibility of achieving nearly complete reduction of lead sulfide, and at the same time not emitting any gas appears to be some version of the precipitation method. A solid reducing agent is used and the products of the reaction are solids or liquids at the temperature of interest.

III. THERMODYNAMICS OF THE REDUCTION OF LEAD SULFIDE WITH IRON

A. Introduction

As mentioned earlier, the reduction of galena with iron appears to offer a good basis for a process to directly reduce lead concentrate to metal without evolution of gaseous reaction products. In the following sections, the thermochemistry of the reduction of galena with iron will be discussed. The need for a suitable flux on the thermochemistry will also be discussed.

B. The System Iron-Sulfur

The iron-sulfur phase diagram is shown in Figure 1, as presented by Levin, Robbins, and McMurdie[22]. The two stable compounds are pyrite (FeS_2) and pyrrhotite (Fe_xS). In equilibrium with metallic iron, pyrrhotite is very close to stoichiometric composition. The thermodynamics of Fe-S melts have been recently discussed by Nagamori[23] and by Schurmann and Henke[24,25], and several other authors.

The thermodynamic properties of FeS have recently been summarized by Robie and Waldbaum[26]. They referred to their FeS as troilite, which is that mineral version of FeS of composition in equilibrium with metallic iron. For the purposes of this work, the thermodynamic properties of FeS are taken from Robie and Waldbaum. Later on, reference will be made to that version of iron sulfide called pyrrhotite, which ranges in composition from $FeS_{1.0}$ to about $FeS_{1.1}$. Since there is some uncertainty as to the exact use of the nomenclature of the iron sulfide minerals, the term pyrrhotite will be generally adopted to refer to "FeS".

C. The System Lead-Sulfur

According to Levin, Robbins, and McMurdie[22], the Pb-S system shows incomplete miscibility in the liquid state. Galena is the only stable compound and has a very narrow composition range. Esdaile[27] determined the lead-lead sulfide miscibility gap over a narrow temperature range (1041 to 1058°C). The phase diagram for the Pb-S system is presented in Figure 2.

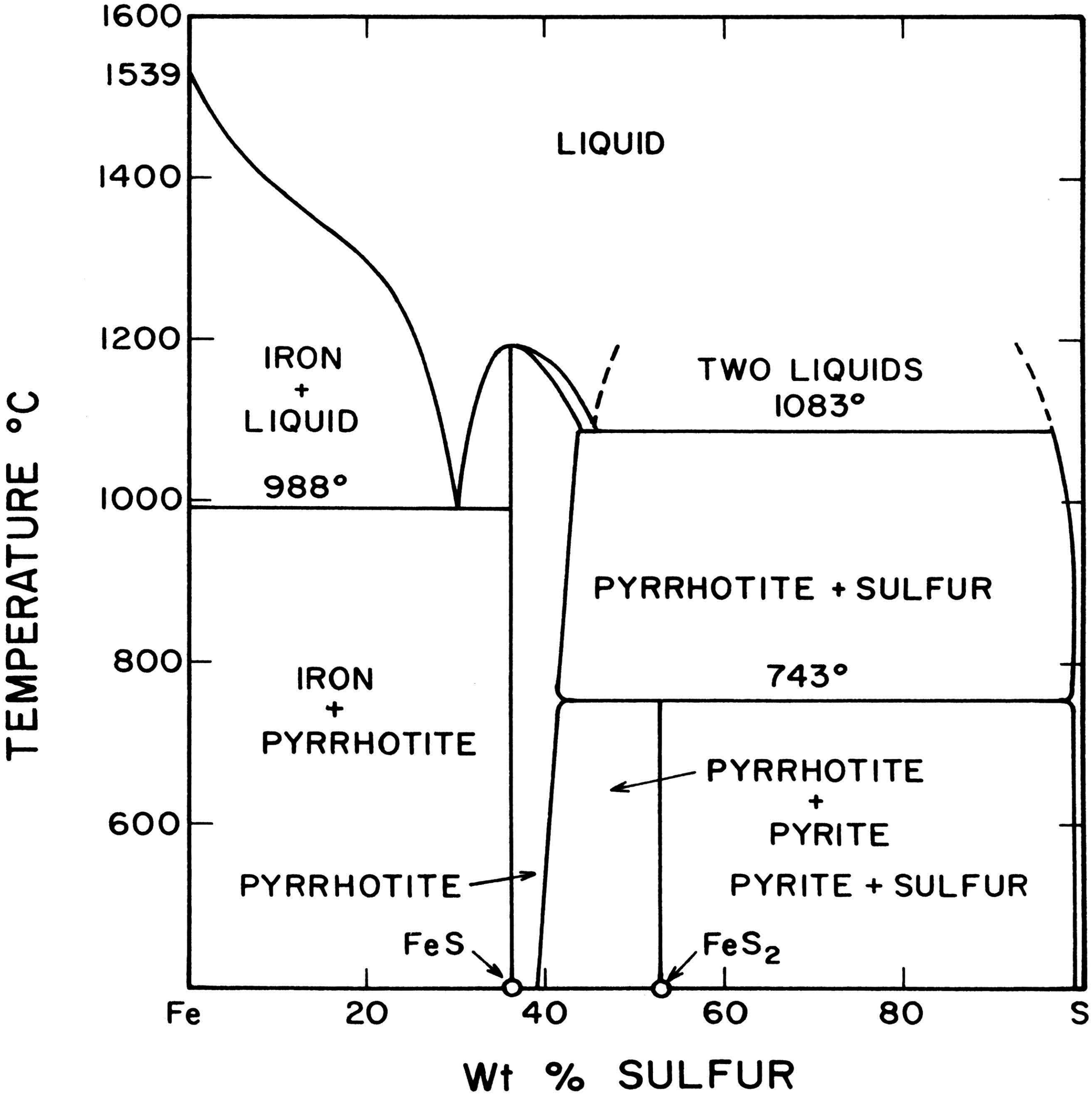

Figure 1. Phase Diagram for the System Fe-S[22]

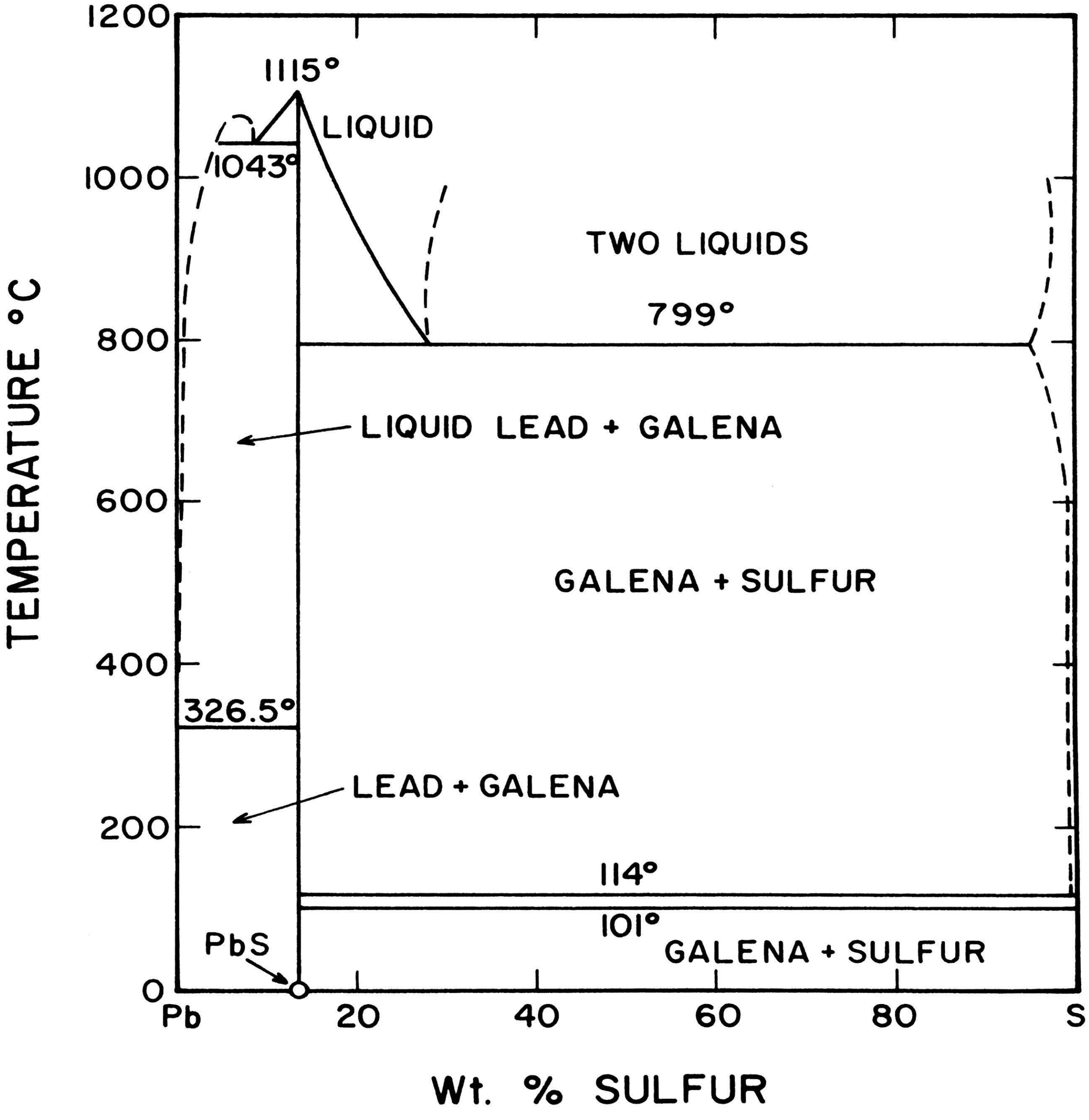

Figure 2. Phase Diagram for the System Pb-S[22]

A recent survey of the thermodynamic properties of lead sulfide was published by Wittung[28]. For purposes of the present work, the free energy of formation of galena given by Thompson and Flengas[29] (determined over the temperature range 800 to 1100°K) will be used:

$$Pb_{1} + 1/2\ S_{2_{g}} \rightarrow PbS_{s} \tag{8a}$$

$$\log K_{f} = 8740/T - 4.92 \tag{8b}$$

D. The System Lead-Iron

For practical purposes, iron and lead are completely insoluble. There is some solubility of lead in liquid iron at higher temperatures, but there is no apparent solubility of iron in liquid lead. The phase diagram for this system was first compiled by Hansen[30] and later by Elliot[31], and Shunk[32].

E. The System Iron-Lead-Sulfur and the Thermodynamics of the Reduction of PbS with Iron

Levin, Robbins, and McMurdie[22] have constructed an isothermal section through the phase diagram at 850°C, which shows no compatibility line between iron and galena. The stable phases in equilibrium with metallic iron will therefore be iron sulfide and metallic lead. This diagram is presented in Figure 3.

When iron is added to galena, the products formed are FeS and metallic lead. The logarithm of the equilibrium constant for the reaction at 1300° and 1400°K are as follows:

$$PbS_{s,1} + Fe_{s} \rightarrow FeS_{s,1} + Pb_{1} \tag{9}$$

$$\log K = 1.38 \text{ at } 1300°K$$

$$\log K = 1.42 \text{ at } 1400°K$$

The activity of Fe and Pb may be set equal to 1. If we assume the FeS to be nearly pure, and hence have an activity close to 1, it is possible to calculate the activity of PbS in the iron sulfide. The activity of PbS at 1300° and 1400°K is:

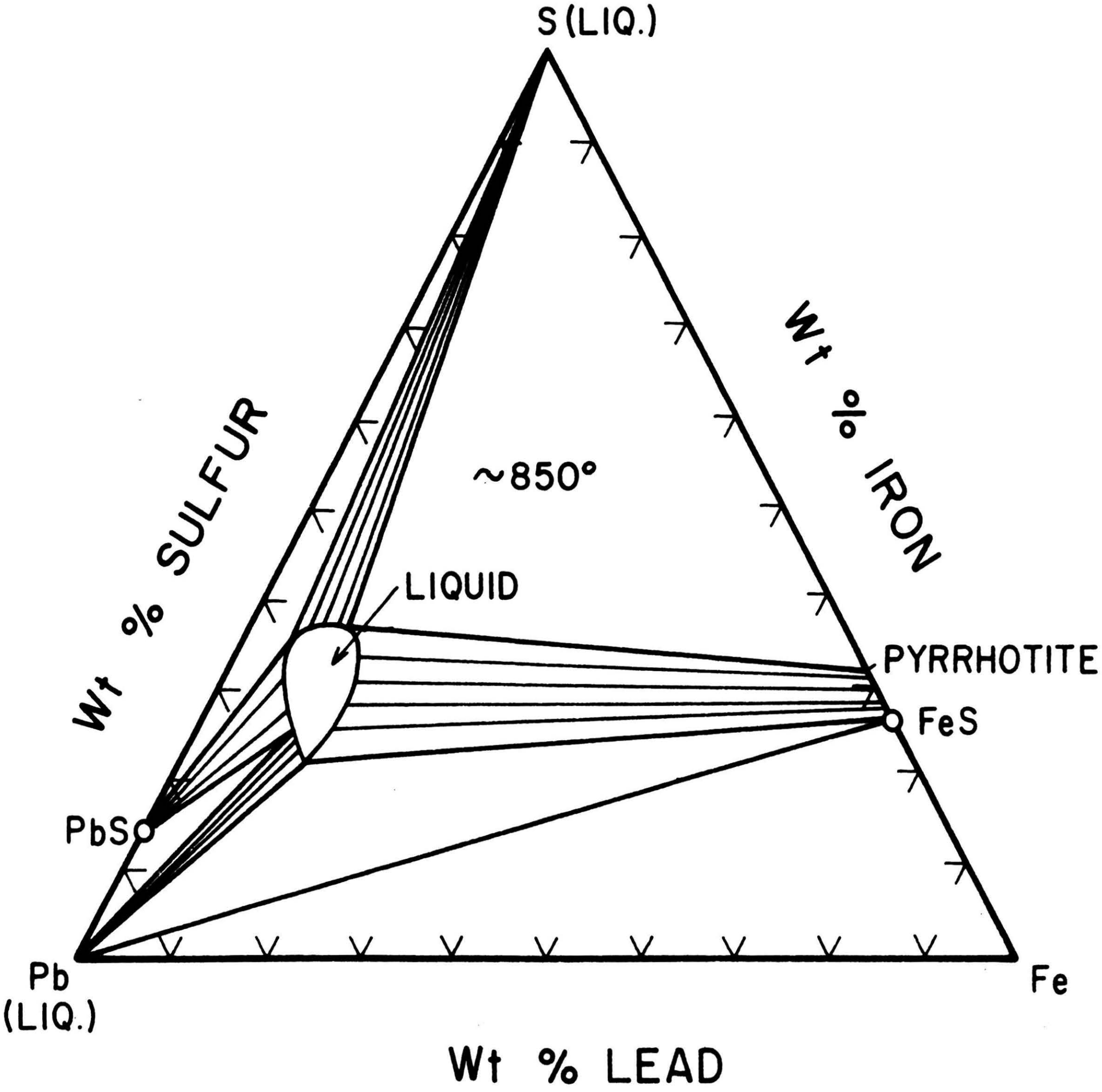

Figure 3. Phase Diagram for the System Pb-Fe-S at 850°C[22]

$$\log a_{PbS} = -\log K_{(9)} \quad (10)$$

Therefore, according to Equation (9) the activity of PbS is 0.042 at 1300°K; and 0.038 at 1400°K.

These relations are indicative of the greater stability of FeS compared to PbS. They also explain the success of the so-called Precipitation Process which was operated using metallic iron as a reducing agent for lead concentrates.

The concentrate also contains small amounts of zinc and copper sulfides. The logarithm of the equilibrium constant for the iron reduction of these sulfides is:

$$ZnS_s + Fe_s \rightarrow Zn_g + FeS_s \quad (11)$$

$\log K = -2.07$ at 1300°K

$$Cu_2S_s + Fe_s \rightarrow 2Cu_s + FeS_s \quad (12)$$

$\log K = -0.63$ at 1300°K

The data for ZnS and Cu_2S was taken from Robie and Waldbaum[26]. Due to the negative values for the logarithm of their equilibrium constant, it is not possible to reduce ZnS and Cu_2S to the pure metals using iron. To recover zinc as a gas at 1 atmosphere from a high zinc concentrate with iron as a reducing agent, the lowest possible temperature is 1660°K from theoretical calculations[33].

F. The System Iron-Oxygen-Sulfur

In some preliminary experiments it was found that the reduction of galena by iron in the absence of fluxes gives poor recovery of lead at reasonable time periods at 1100°C. This is mainly caused by the incompletely fusible reaction products, and possibly by inadequate driving force for the reaction to proceed completely to the right. Therefore if iron is to be used as a reducing agent for galena it is desirable to accomplish two things: lower the melting point of the reaction products and lower the activity of FeS. If a suitable flux can be found to lower the activity of FeS to one half, the activity of PbS would be 0.021 at 1300°K and 0.019 at 1400°K. Lowering the activity of PbS in this matte implies that its solubility would be lowered as well.

To some extent this was accomplished in the Salt Process, described earlier. For more effective reduction and recovery of lead sulfide by iron, something should be added to lower the activity and the melting point of FeS. From phase diagrams and calculations it will now be shown that iron oxide is such an ingredient. In an attempt to understand the effect of iron oxide on the Fe-FeS system, a study of the phase equilibria and thermodynamics of the Fe-S-O system was undertaken.

The part of the ternary diagram for the Fe-S-O system that is in equilibrium with metallic iron is shown in Figure 4, which is based on the diagram of Hilty and Crafts[34]. Above the eutectic temperature of 920°C, the molten phase is limited at high oxygen content by equilibrium with wustite, and at high sulfur content by equilibrium with pyrrhotite. Iron oxide thus lowers the solidus temperature of Fe-S melts. This may be seen more clearly by a phase diagram for the system FeO-FeS which will be presented later. The point labeled "matte composition" will be discussed later.

Bog and Rosenqvist[35] studied the thermodynamics of iron oxysulfide melts and determined the activities of FeO and FeS in iron oxysulfide melts at 1120°C (1393°K). Their results are shown in Figure 5. The probable relationship between the activities of iron oxide and iron sulfide at iron saturation is shown in Figure 6, which was based on data taken from Figure 5. Along the iron saturation line equal intervals of FeS and FeO activities were extrapolated, and a probable curve which relates these activities was drawn.

Turkdogan and Kor[35] gave plots of oxygen and sulfur potentials vs. temperature for six condensed phases: iron, wustite, magnetite, pyrrhotite, liquid oxysulfide, and metallic liquid. The latter phase is not present at temperatures of interest to this work. These graphs were replotted as log p_x vs. temperature. Figure 7 shows the variation of log p_{s2} vs. temperature, and Figure 8 shows the variation of log p_{O_2}. For the univariant iron-wustite-liquid (line "c") at 1100°C,

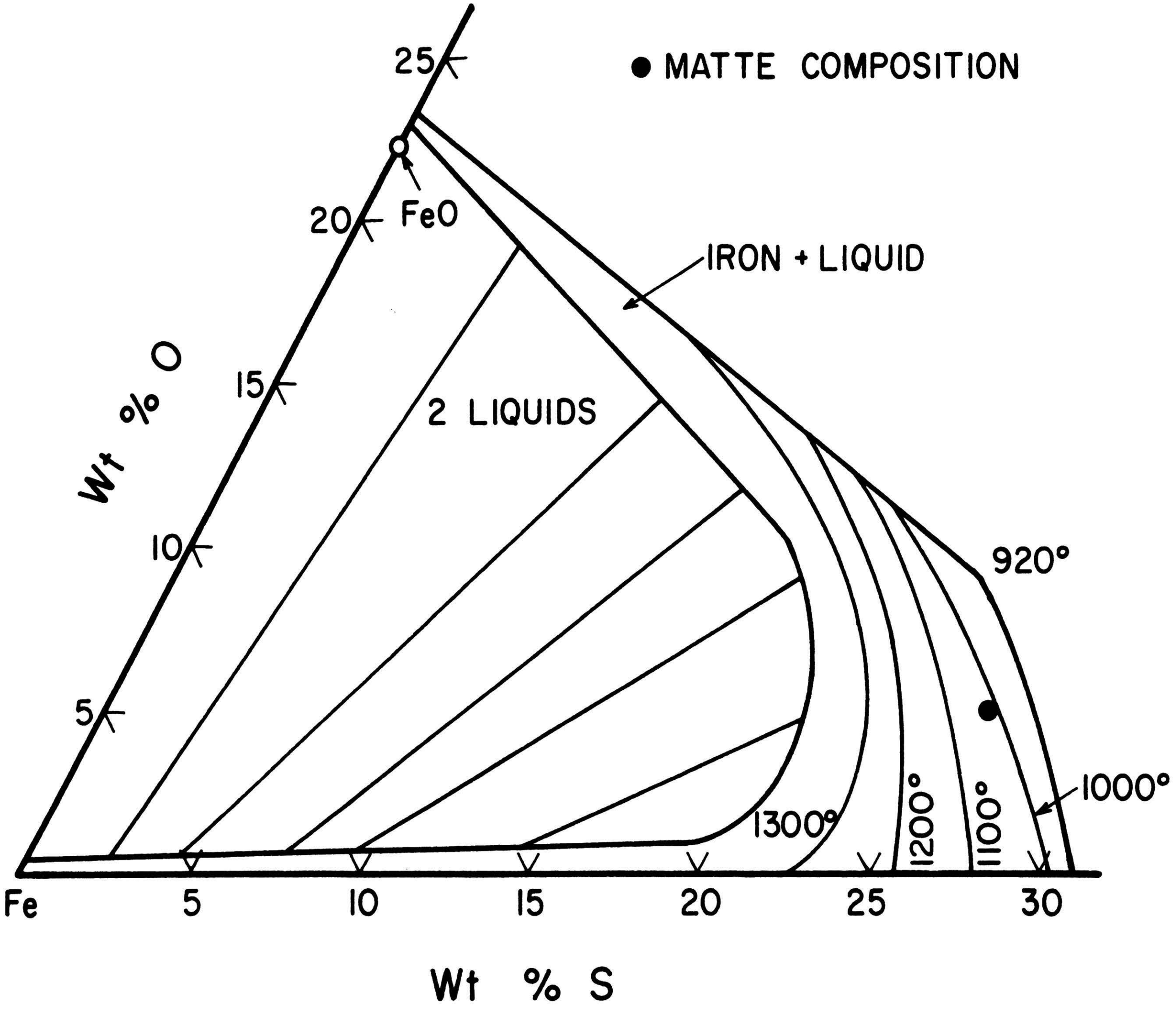

Figure 4. Phase Diagram for the Fe-O-S System (Dot is the Matte Composition from Chemical Analysis)[34]

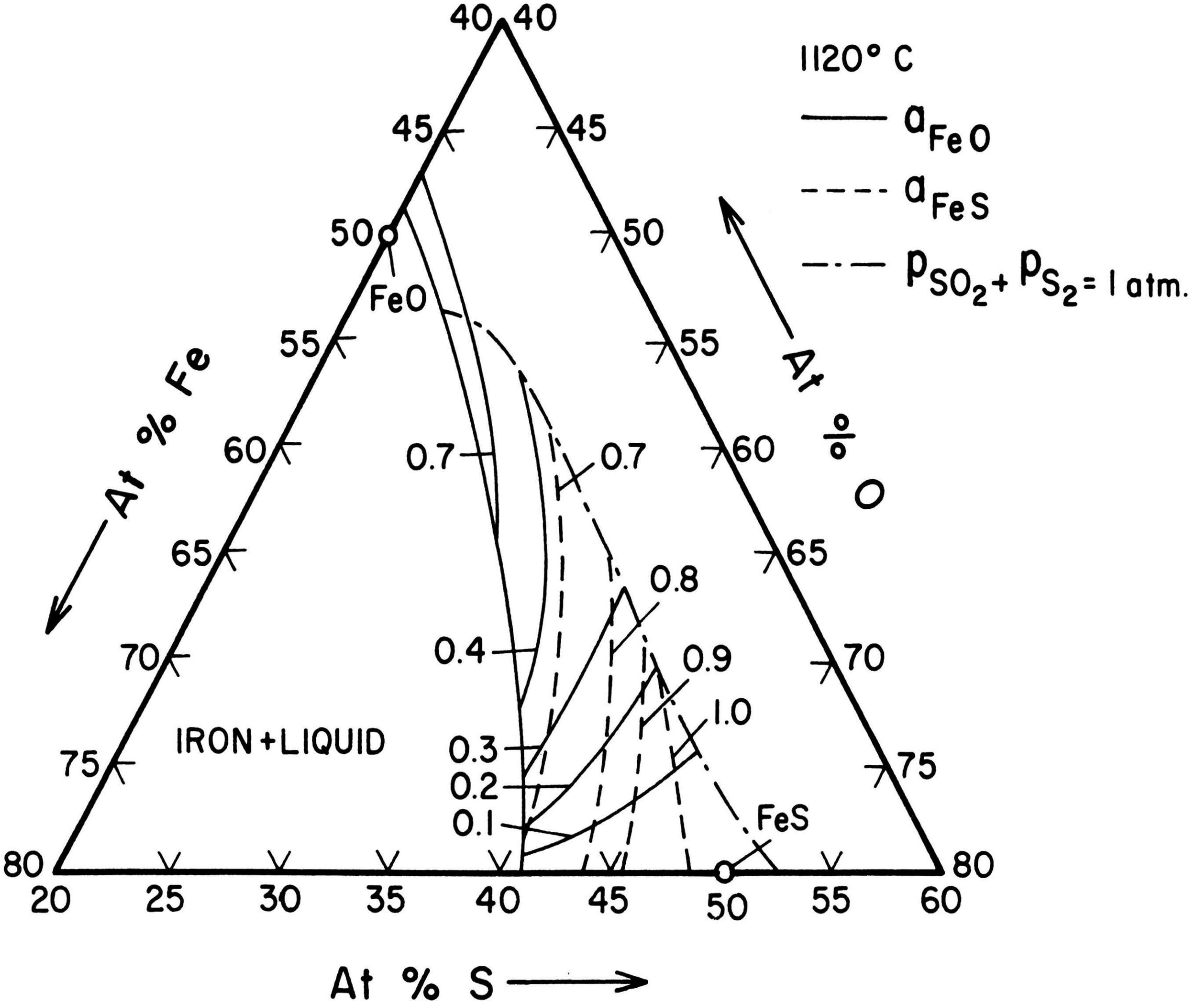

Figure 5. Activities of FeO and FeS in the Liquid Oxysulfide Region[35]

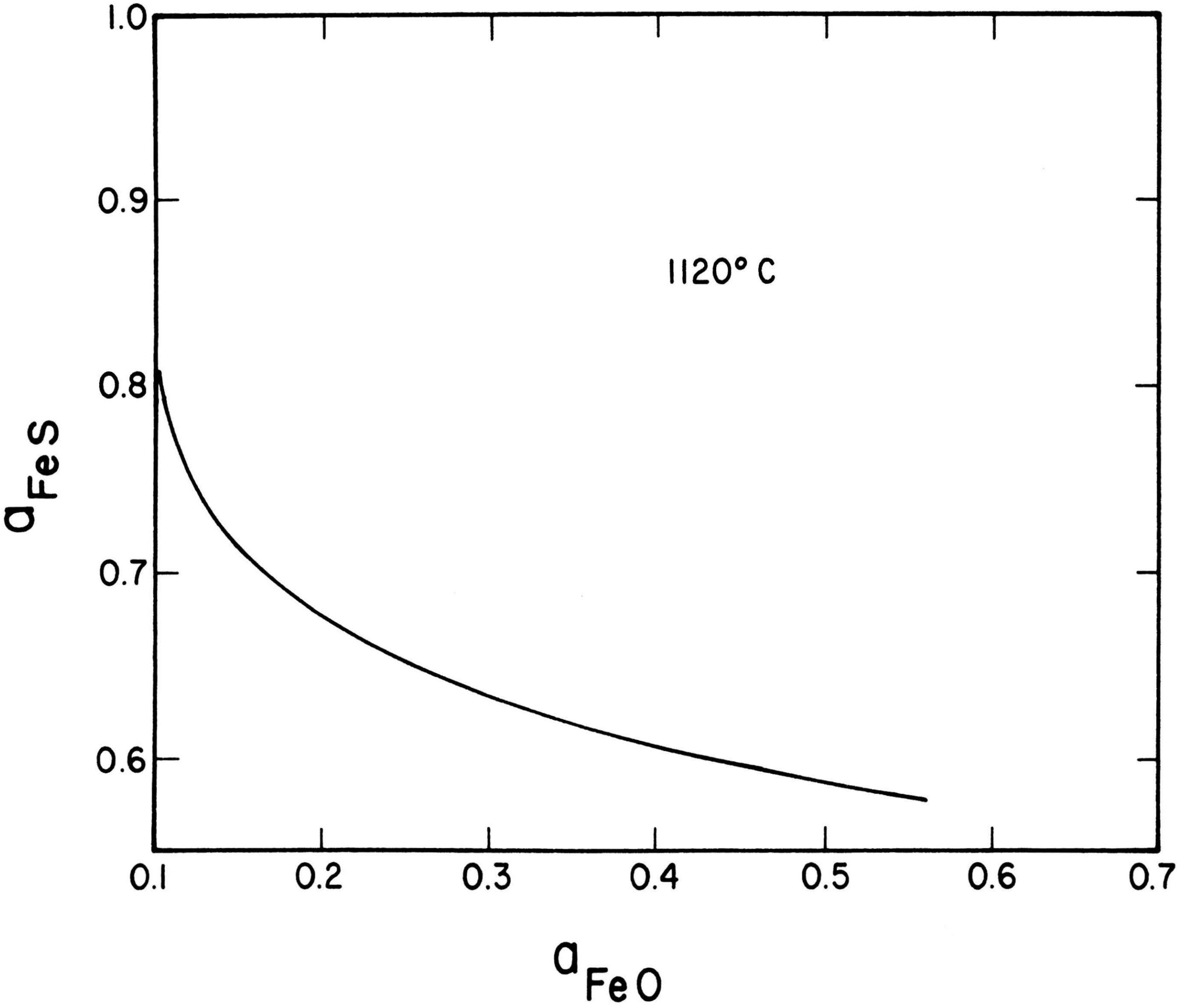

Figure 6. Probable Relationship Between FeO and FeS Activities in Equilibrium with Metallic Iron

the pressure of sulfur is very low ($10^{-6.5}$ atm). At the same temperature the oxygen pressure for this univariant is $10^{-13.3}$ atm.

If the above data is compared to the p_{S_2} for the Cu-Cu_2S equilibria at the same temperature, Cu_2S should be the stable phase. For the equilibria between ZnS and ZnO, the following equation must be considered:

$$ZnS + 1/2\ O_2 \rightarrow ZnO + 1/2\ S_2 \qquad (13)$$

$$\log K = +2.89 \text{ at } 1300°K^{(26)}$$

If we insert the values for p_{O_2} and p_{S_2}, just mentioned, the reaction has a tendency to go to the left, thus ZnS will be the stable phase at this particular temperature.

The data of Figure 7 and 8 may be combined to plot a log p_{SO_2} diagram. Figure 9 shows the results of this combination. The value of log K for formation of SO_2 was taken from Robie and Waldbaum[26]; the log p_{SO_2} along the iron-wustite-liquid oxysulfide phase boundary varies from -6.3 at 1400°K to -8.2 at the ternary eutectic composition (1193°K). Figure 9 shows that any reduction process in equilibrium with metallic iron and an iron oxysulfide phase below 1400°K is in equilibrium with an extremely low SO_2 pressure. A phase diagram for the system iron oxide-iron sulfide in equilibrium with metallic iron[35] is shown in Figure 10. Isobars of p_{SO_2} were calculated from data taken from Figure 9 and then plotted on Figure 10.

G. Summary and Conclusions

The thermodynamic calculations show that iron should be an effective reducing agent for the PbS in a lead concentrate. The phase diagrams show that iron oxide is an effective flux for FeS, and that the activity of FeS may be lowered significantly by iron oxide. In equilibrium with metallic iron, the only gases of any consequence are S_2 and SO_2, and their partial pressures are less than 10^{-6} atm.

Another way to visualize how the fluxing of FeS might increase lead reduction is by means of a phase diagram of the Fe-Pb-S-O system. This is shown in Appendix C.

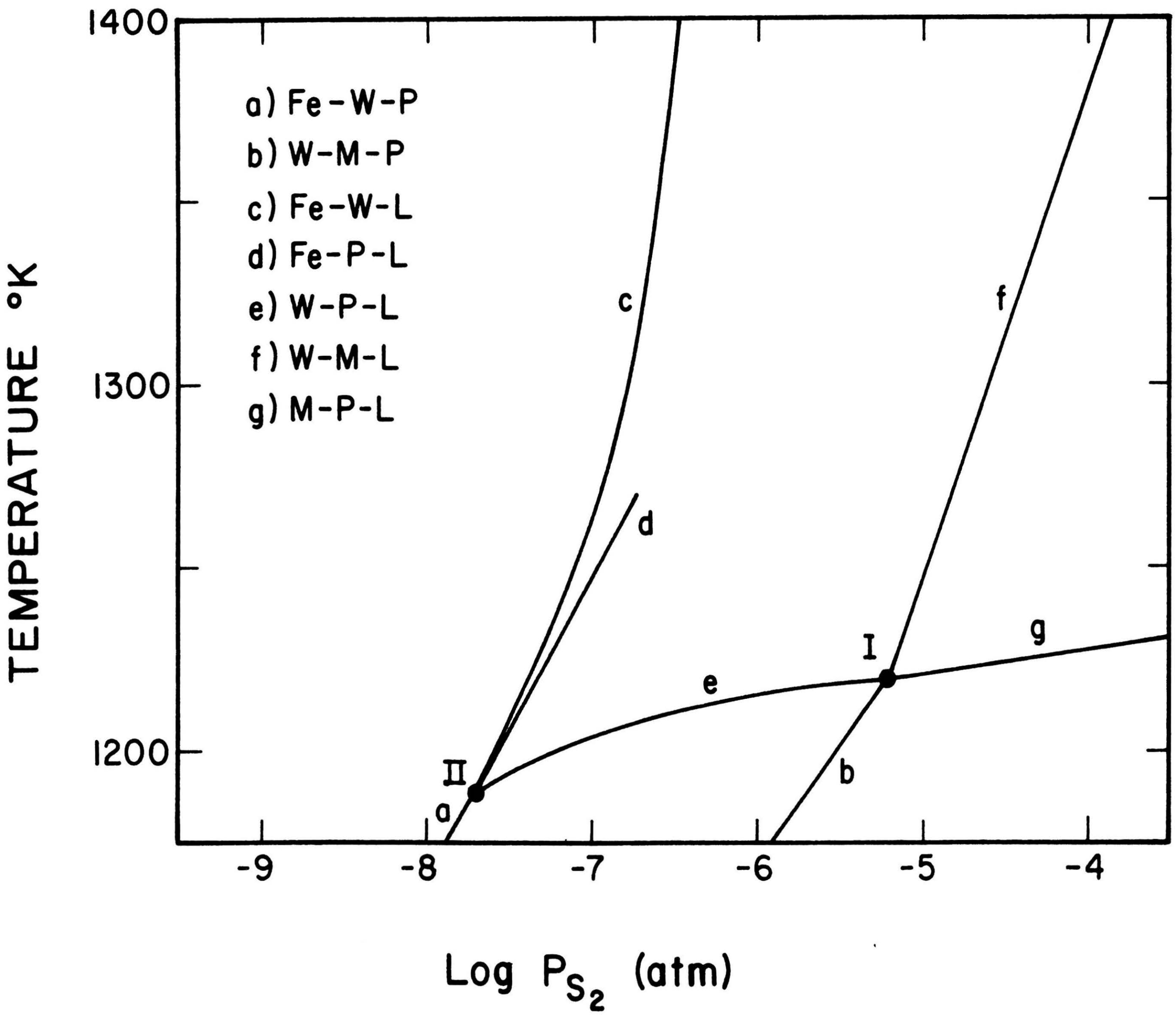

Figure 7. Sulfur Potentials for Univariant Equilibria in the Fe-O-S System (Fe=Iron, P=Pyrrhotite, W=Wustite, M=Magnetite, L=Liquid)

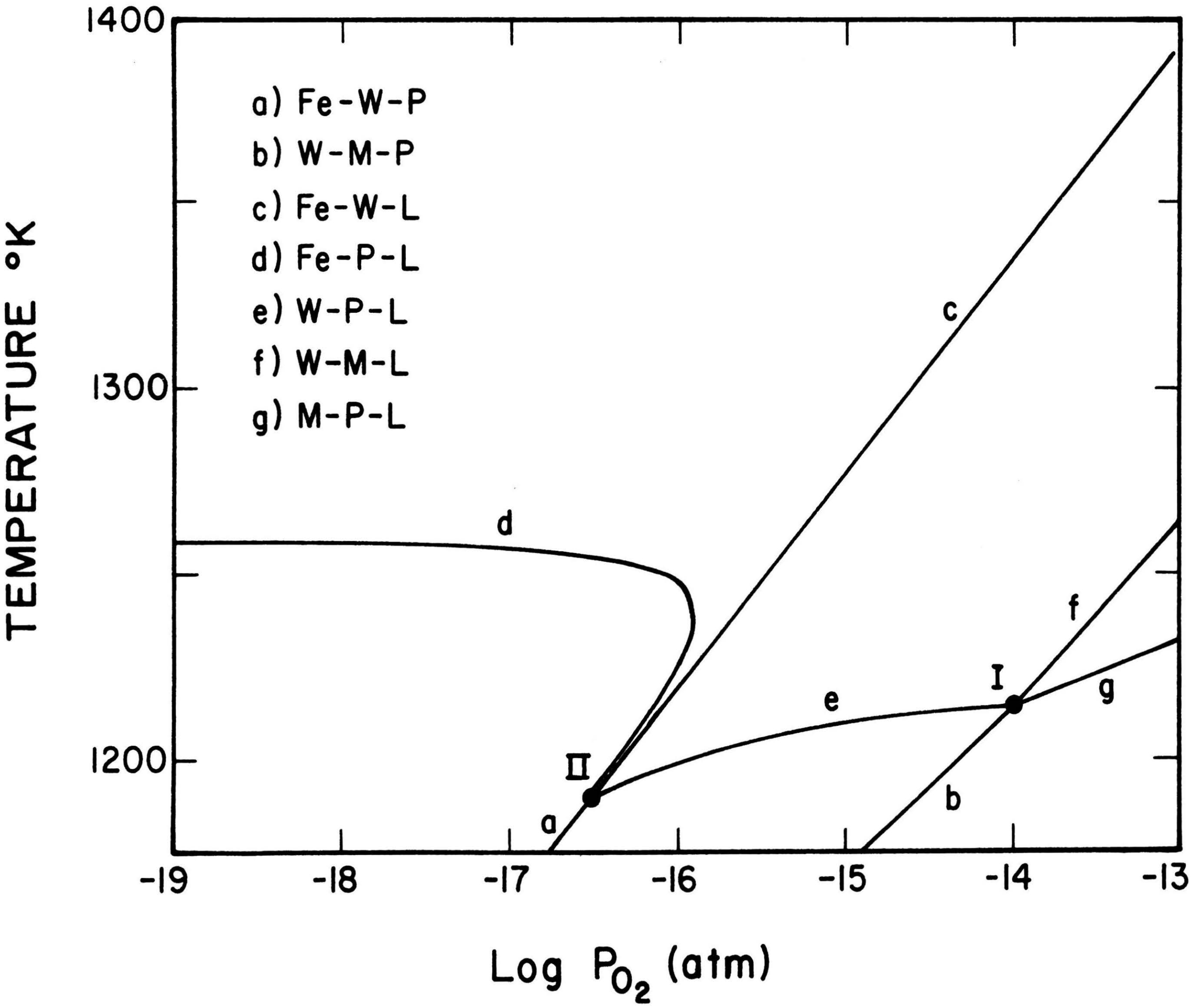

Figure 8. Oxygen Potentials for Univariant Equilibria in the Fe-O-S System (Fe=Iron, P=Pyrrhotite, W=Wustite, M=Magnetite, L=Liquid)

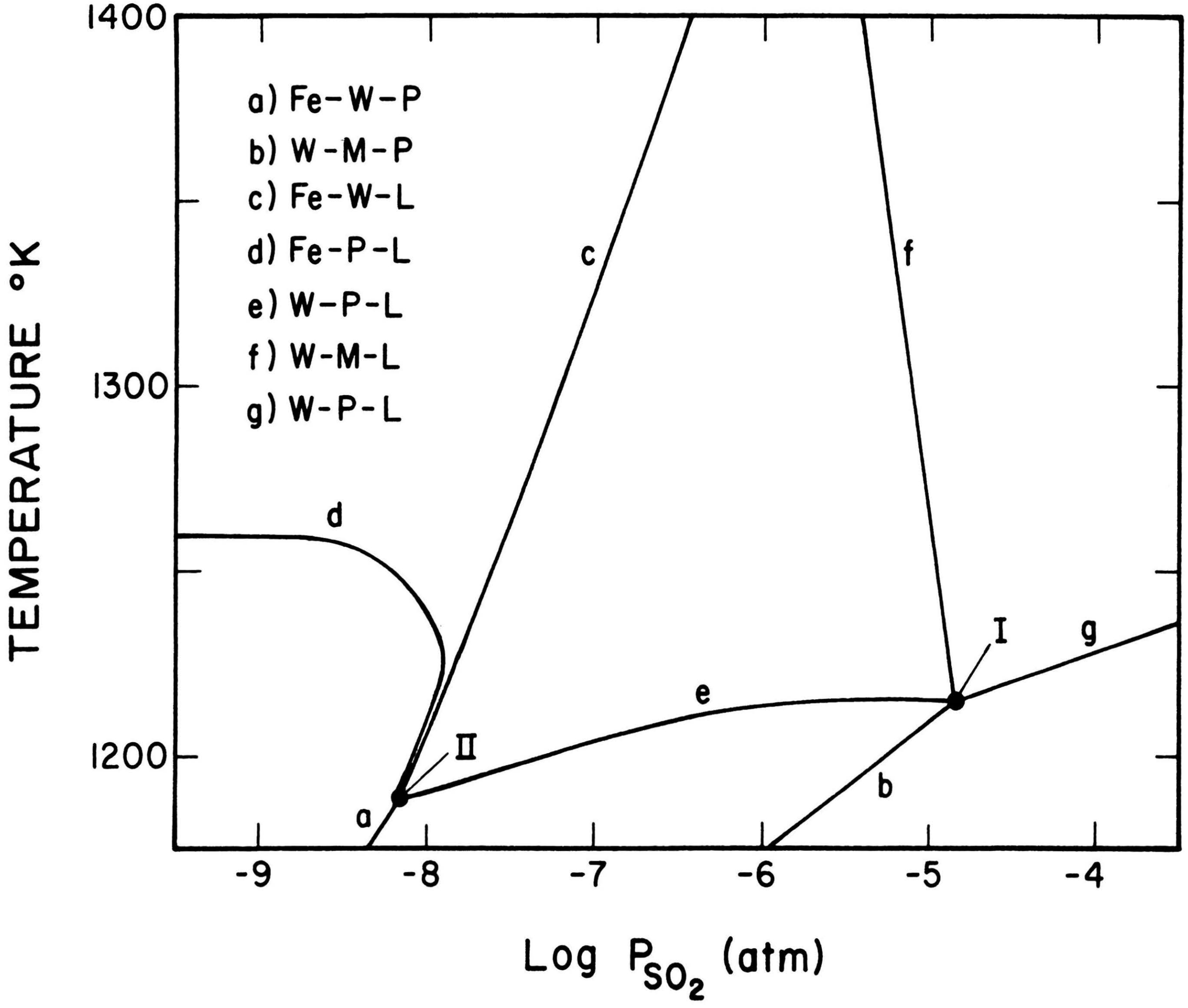

Figure 9. Sulfur Dioxide Potentials for Univariant Equilibria in the Fe-O-S System (Fe=Iron, P=Pyrrhotite, W=Wustite, M=Magnetite, L=Liquid)

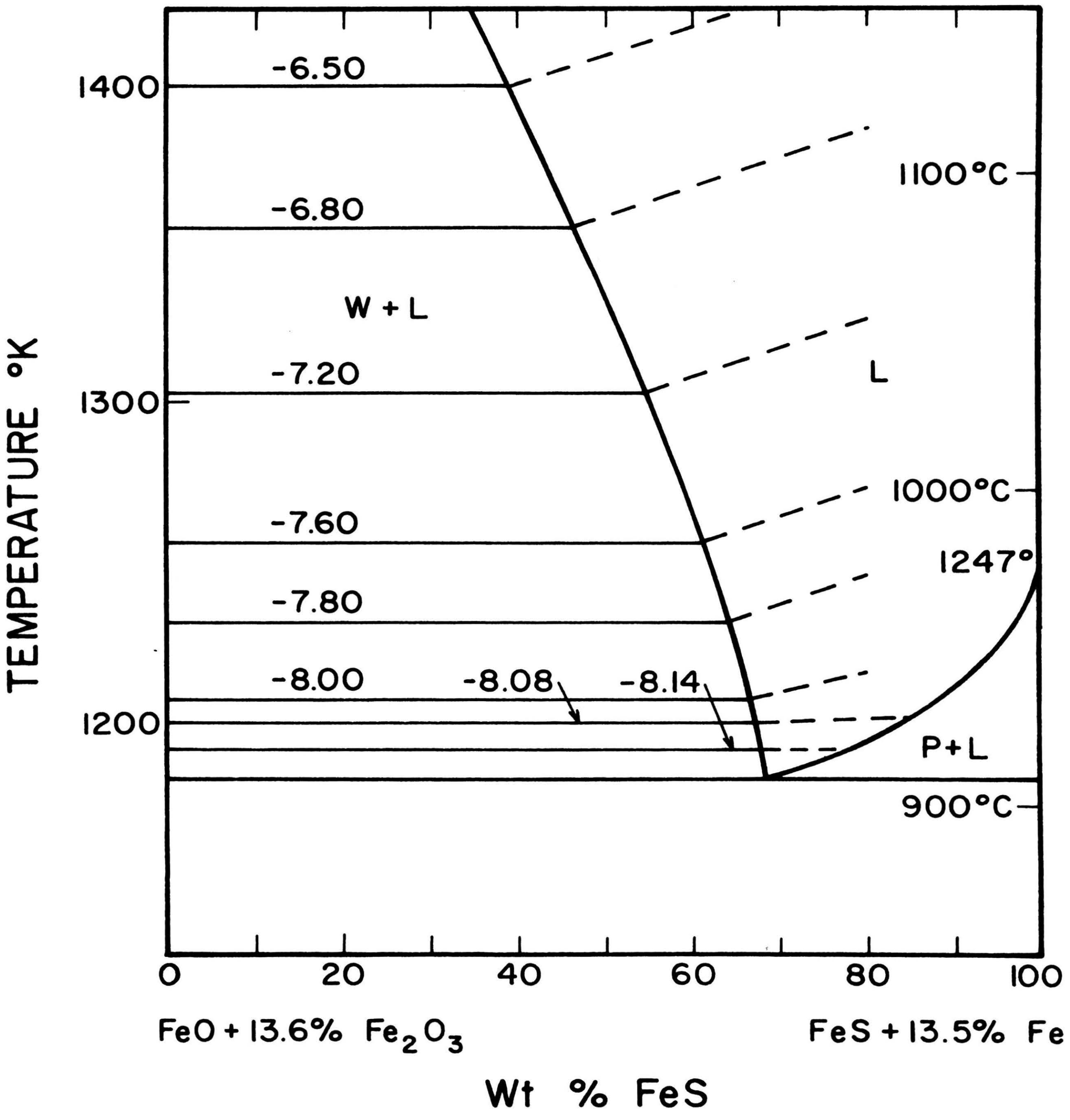

Figure 10. The FeO-FeS System in Equilibrium with Metallic Iron with SO_2 Isobars. (W=Wustite, P=Pyrrhotite)

IV. EXPERIMENTAL METHOD

A. Furnaces and Temperature Control

The samples for the experimental smelting were fired in a large muffle furnace heated by silicon-carbide elements. The furnace temperature was controlled by a millivolt pyrometer and a chromel-alumel thermocouple.

For the SO_2 measurements and phase identification smelting runs, a tube furnace heated by silicon-carbide elements was used. The furnace tube was mullite, 5.4 cm I.D. by 100 cm long. The top of the tube was sealed by a rubber stopper with a small glass T-tube, which had the dual role of serving as a gas inlet and as a support for the sample holder. The temperature of the furnace was controlled by a millivolt pyrometer with an accuracy of ± 2°C. The control thermocouple was a Pt/Pt-13% Rh thermocouple inserted near the elements at the hot zone of the furnace. The sample temperature inside the tube was measured with a chromel-alumel thermocouple. A sketch of the tube furnace is shown in Figure 11.

B. Atmosphere Control

Depending on the furnace used and the purpose of the experiment, the following different atmosphere control procedures were used: In the muffle furnace, in order to keep air from contacting the sample, the iron sample crucible was placed in a larger fireclay crucible and an iron lid was put on the iron sample crucible. Then charcoal was poured into the remaining volume of the fireclay crucible with one additional iron lid. The top of the fireclay crucible was then covered with a clay lid. The assembly of the fireclay and sample crucible is shown in Figure 12. During heating a small piece of cardboard placed in the bottom of the fireclay crucible evolved gas to purge air from the crucible. This experimental arrangement kept the iron crucible from oxidizing and hence was judged to be an effective barrier to oxygen.

For the tube furnace, the inlet gas was high purity nitrogen supplied by the Matheson Company. The rate of the nitrogen flow was maintained at 10 cc per minute.

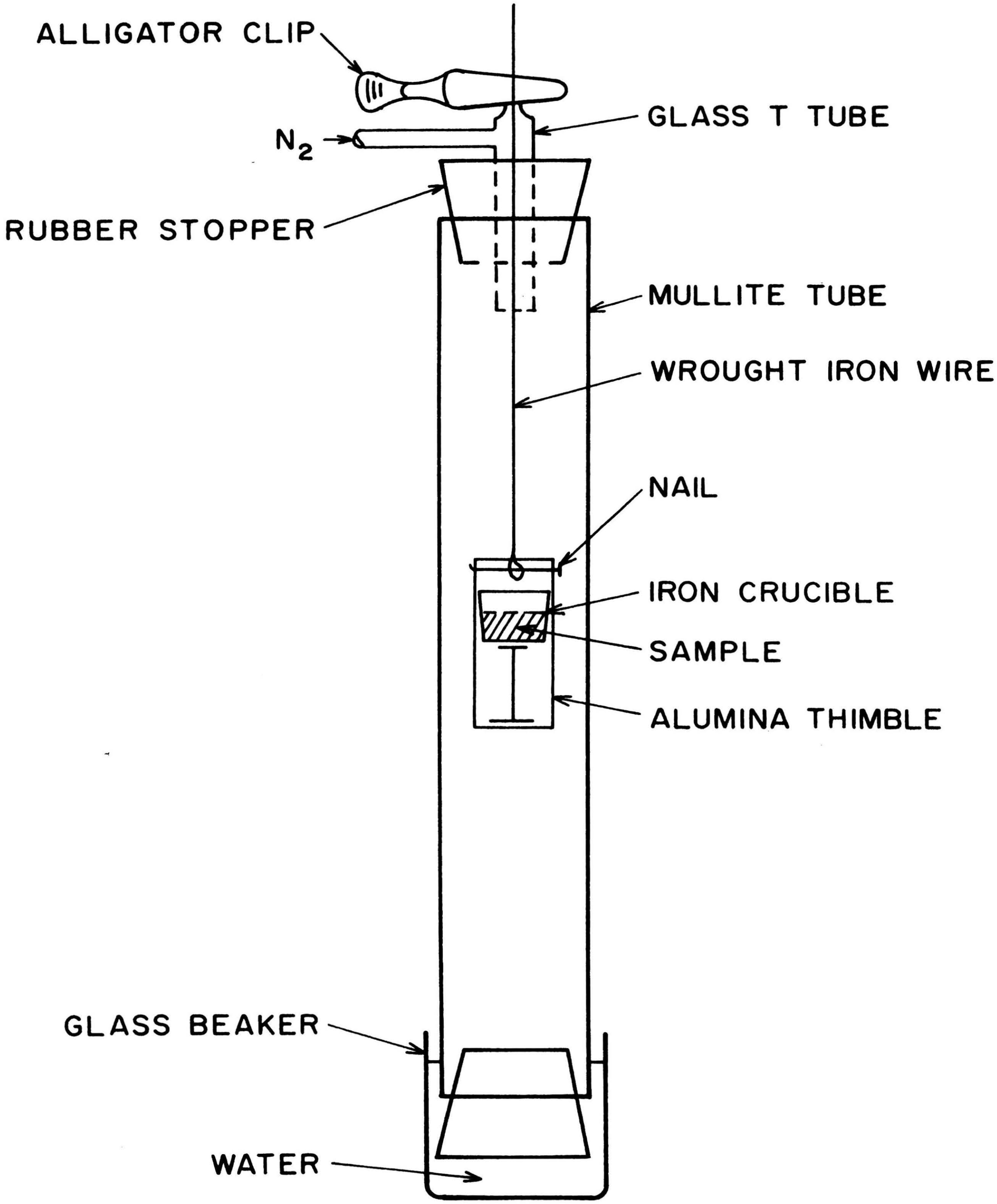

Figure 11. Sketch of Tube Furnace and Sample Arrangement

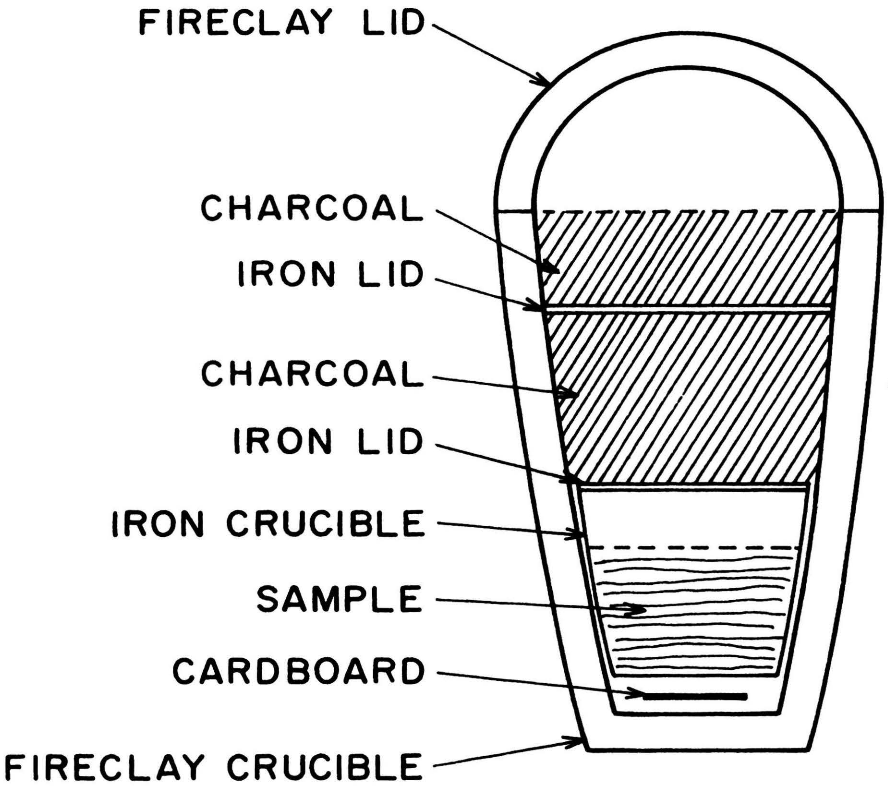

Figure 12. Sketch of Sample Arrangement in the Muffle Furnace

C. Preparation of Starting Materials

The lead concentrate used in all experiments was a regular mill concentrate containing 74.2% lead, and was provided by the Missouri Lead Operating Company. This concentrate was analyzed by several companies, and the average is presented in Table I. For most experiments, the concentrate was simply dried in an oven for 24 hours at 200°C.

Table I. Chemical Analysis of Lead Concentrate

Weight	Wt. %
Pb	74.20
Zn	1.70
Cu	1.69
Fe	2.60
S	15.60
CaO	1.00
MgO	0.40
SiO_2	0.30

The powdered iron was an electrolytic grade of particle size -100 mesh. The iron oxides Fe_2O_3 and Fe_3O_4 were reagent grade of commercial purity. They were dried at 150°C for 8 hours.

D. Smelting Procedure

Mixtures of lead concentrate, oxide and iron were prepared by first weighing each ingredient within ± 0.02 gm. The ingredients were blended, then poured in an empty bottle and shaken for five minutes in order to mix the sample. The mixture was put into a 25 or 30 cc iron crucible and tapped on the table to settle the contents together. The crucible was then inserted into a large fireclay crucible as described earlier. The covered fireclay crucible was put into the muffle furnace for different temperatures and times, then removed to cool. The iron crucible was cut open with a small saw, and the metallic lead and other phases carefully removed. The lead was usually in the form of an ingot in the bottom of the crucible. Sometimes a glob or two of lead would be found on the inside of the upper part of the crucible. This glob was removed and added to the ingot, and counted as recovered lead.

Some original experiments were done in porcelain crucibles. However, in order to keep out foreign material, iron crucibles were adopted for all subsequent runs.

In the smelting experiments the charge often swelled up to fill or sometimes overflowed the iron crucible and at the same time a grey smoke was evolved. In an attempt to eliminate this swelling and smoking, the concentrate was given a further cleaning treatment to remove the flotation reagents left on the concentrate and any remaining moisture. The following steps were carried out to clean the concentrate.

1. The concentrate was washed with acetone in an ultrasonic cleaner for two hours.
2. It was washed again with methyl ethyl ketone in an ultrasonic cleaner for two hours.
3. It was then heated for eight hours in a vacuum oven at 180°C.

These steps were found quite adequate to eliminate the swelling tendency and almost all the smoke in the concentrate. This cleaned concentrate was used in all experiments carried out in the tube furnace.

In order to have enough material for phase identification, samples of 120 to 180 grams of concentrate, (about 4 to 6 times the amount usually used in the smelting runs) were reduced in a tall welded crucible. The crucible was made by welding a 7.5 cm mild steel tube to the top of the regular 25 cc iron crucible. After 1-1/2 hours in the tube furnace at 1100°C, the crucible was cooled down slowly, then sectioned in half along the long axis using a band saw. Pictures of the sample were taken with a Polaroid camera.

X-Ray patterns of the non-metallic phases were obtained by using the powder method[37]. A Norelco X-Ray diffractometer with Fe tube and Mn filter were used. In all experiments a standard Debye-Scherrer camera was employed. Each sample was ground to -200 mesh and exposed for 10 hours.

E. Sulfur Dioxide Determination

In order to determine the SO_2 evolved during the smelting process, the following method was used: A syringe was attached to the outlet gas tube from the furnace. A cigarette filter in the line filtered out part of the small amount of smoke that was evolved. Nitrogen was used as a carrier gas through the furnace which was then passed through a Kitagawa SO_2 detector tube. Two types of these tubes were used: type D with a range of 1 to 80 ppm and type C with a range of 5 to 300 ppm (by volume). The accuracy of the readings was ± 10%. Since about 80 ppm of SO_2 was present, the type C tube was usually employed. The gas was sampled by a 35 cc capacity syringe, and inserted into the detector tube, which then changed color. The tube then was compared to a concentration chart to determine SO_2 content.

F. Chemical Analysis

Chemical analysis of the reaction products was carried out for S, Fe, Cu, Pb, and Zn by the St. Joe Minerals Corporation laboratories in Herculaneum, Missouri. The Ca, Mg, Si, and O analyses were carried out by Union Carbide Corporation using a neutron activation technique.

V. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Introduction

The present chapter contains first a brief discussion of the experimental results of some preliminary work on the direct reduction of lead sulfide. The chapter then presents and discusses the direct smelting experiments done for the thesis. The preliminary work is presented in the form of tables in the Appendix, and the thesis work is presented as graphs in the text and tables in Appendix B.

B. Preliminary Work

Prior to the present thesis work, some preliminary experiments on the direct reduction of lead sulfide were carried out in the UMR Metallurgical Engineering Department by several students under the supervision of Dr. Arthur E. Morris. Metallic iron was used as the reducing agent, and different fluxes were examined to determine their effectiveness in increasing the yield of metallic lead.

The experiments covered a wide range of temperatures and flux combinations, and the results were presented in internal unpublished reports. A brief summary of the preliminary work is as follows: attempts to reduce a lead concentrate using iron without a flux gave yields less than 60%. Different types of iron oxide bearing materials were tried as fluxes, including a steel plant flue dust. The tests showed that the proper flux, iron and concentrate ratios could result in good recoveries of lead. A thermal anomaly was noted on heating up a mixture of concentrate, flux and iron, which indicated that the initial reaction temperature was approximately 1000°C. A more complete summary of the preliminary results is presented in Appendix A.

C. Direct Smelting Experiments

The experimental results of the direct smelting tests are presented below in the form of graphs, and tabulated in Appendix B. The SO_2 measurements, chemical analyses and phase determination results are presented in the form of tables in this chapter. During the experiments, variable amounts of concentrate, iron and fluxes were used for different runs. In order to present the results on a uniform basis, these weights were all recalculated on a basis of 100 parts by weight of concentrate.

1. Smelting of Concentrate Using Fe_2O_3 as Flux

a. Results

The first objective of the work was to investigate the effect of temperature and time on the reduction of PbS from the concentrate with a given proportion of concentrate, flux, and iron; Fe_2O_3 was used first as the oxygen bearing flux. Mixtures of concentrate, Fe_2O_3 and iron in the ratio: 100/7.5/27.5 were reacted at 1000°, 1050°, and 1100°C for time periods of 1/2 to 1-1/2 hours. The above proportion was selected on the basis of the preliminary experiments as a proportion which was close to that which would give the maximum recovery of lead. Figure 13 shows the results of this first series of smelting tests which corresponds to Table IXa in Appendix B. The lead weight reported is the sum of the ingot weight, plus the weight of any globs of lead that had adhered to the inside wall of the crucible.

After about one hour the lead reduction seemed to be nearly complete. The matte was porous and perhaps incompletely melted at 1000°C. The matte showed less porosity as the smelting temperature was raised to 1100°C. A black sintered spongy material that did not appear to have melted was also present in all samples. This black spongy material was usually found on top of the matte or partially imbedded in the top of the matte. A photograph of a typical smelted sample cut in half is shown in Figure 14.

In many samples small particles of metallic lead (prills) were found in the matte or sponge. Since the prills were not weighed (except in certain later runs), the actual amount of reduced lead was always somewhat more than that reported. On the basis of the first series of runs, a somewhat arbitrary selection of 1 hour at 1100°C was chosen as the time and temperature for investigating the effect of changing the amount of flux and iron.

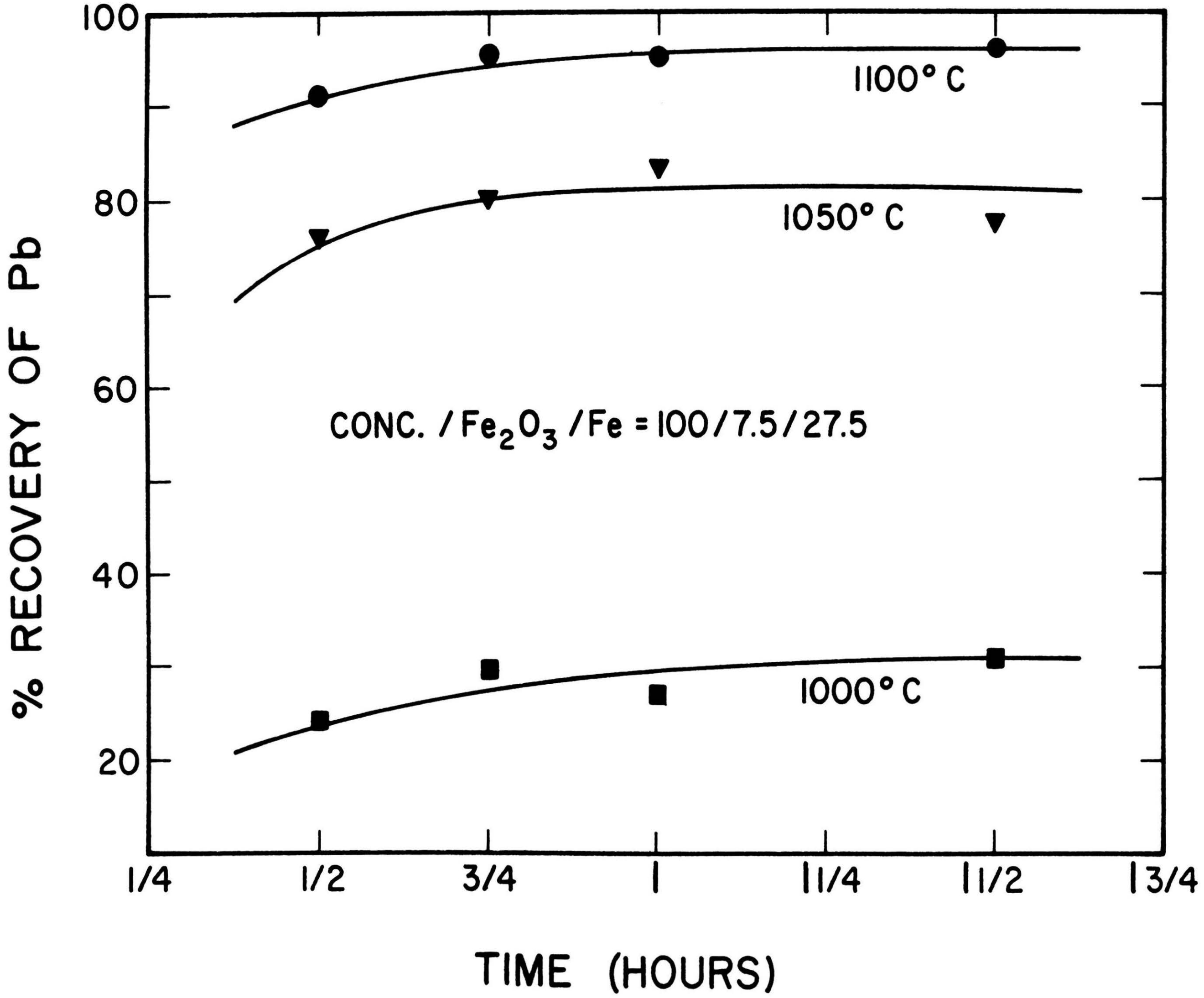

Figure 13. Comparison of Recovery of Lead at Different Times and Temperatures

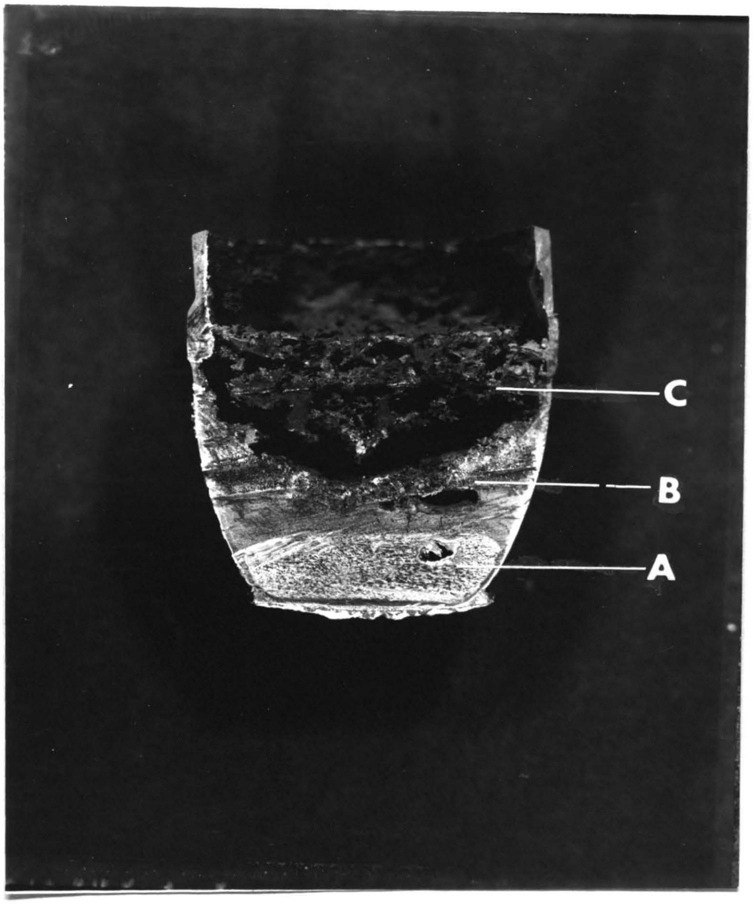

Figure 14. Photograph of Sectioned Sample after Smelting (A=Metallic Lead, B=Matte, C=Spongy Material)

The effect of amount of Fe_2O_3 on lead recovered was then investigated and the results are shown in Figure 15 (Table IXb). The maximum recovery occurred at about 10.8 grams of Fe_2O_3. This amount was then used in the next set of experiments, in which the effect of iron on lead recovery was varied. In all of the experiments low porosity of the matte was noticed.

For a fixed amount of Fe_2O_3 (10.8 gm), the effect of iron content in the mixture was studied next. From 18 to 34 grams of iron was added, as shown in Figure 16 (Table IXc). There was high consumption of iron from the crucible for the three lowest iron runs. After the maximum recovery was attained the matte showed slightly increased porosity.

b. Discussion

At temperatures of 1000° and 1050°C, the recovery of lead is low probably due to a combination of several factors: incomplete reaction of galena and iron, part of the lead remained in the matte, and incomplete fusion of the matte. On the other hand it is seen that at 1100°C, over 95% recovery of lead is possible within an hour. Figures 15 and 16 show that both the amount of iron and Fe_2O_3 have an important effect on the recovery of lead. The maximum recovery of lead for the compositions studied was found at a ratio of concentrate/Fe_2O_3/Fe of about 100/10.8/26. For iron contents below about 25 gm, the reaction apparently does not go to completion. For contents over 25 gm all the PbS is probably reduced, but some metallic lead is retained in the matte as small prills. The reason why excess iron causes lead retention in the matte is not known.

2. Smelting of Concentrate Using Fe_3O_4 as Flux

a. Results

Experiments were conducted to investigate the behavior of magnetite as the oxygen bearing flux, since large amounts of magnetite concentrate are available from iron ore processing plants in southeast Missouri. The recovery of lead as a function of time was studied in the range of 1/2 to 1-3/4 hours for a concentrate/Fe_3O_4/Fe

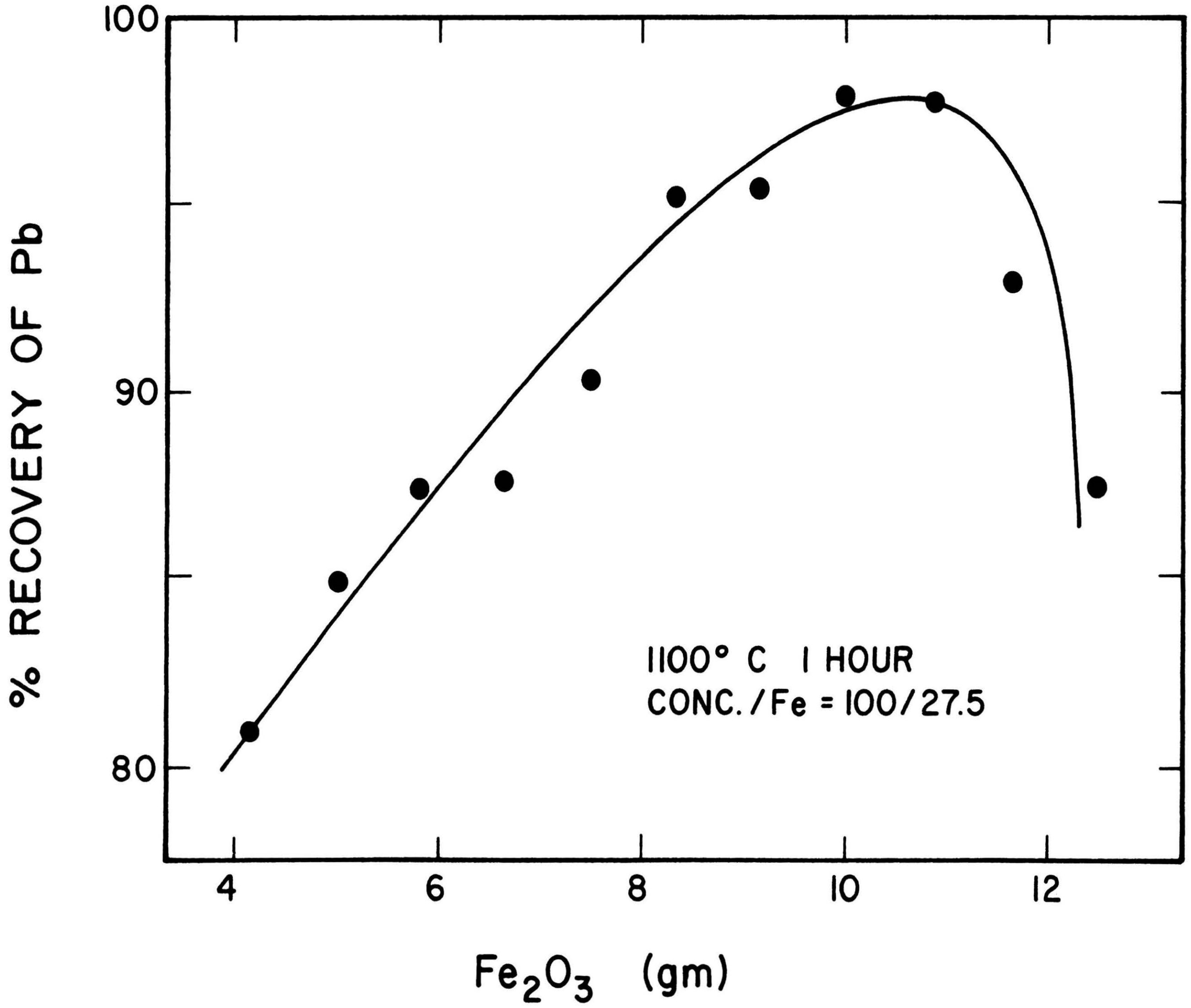

Figure 15. Recovery of Lead vs Fe_2O_3 as Flux

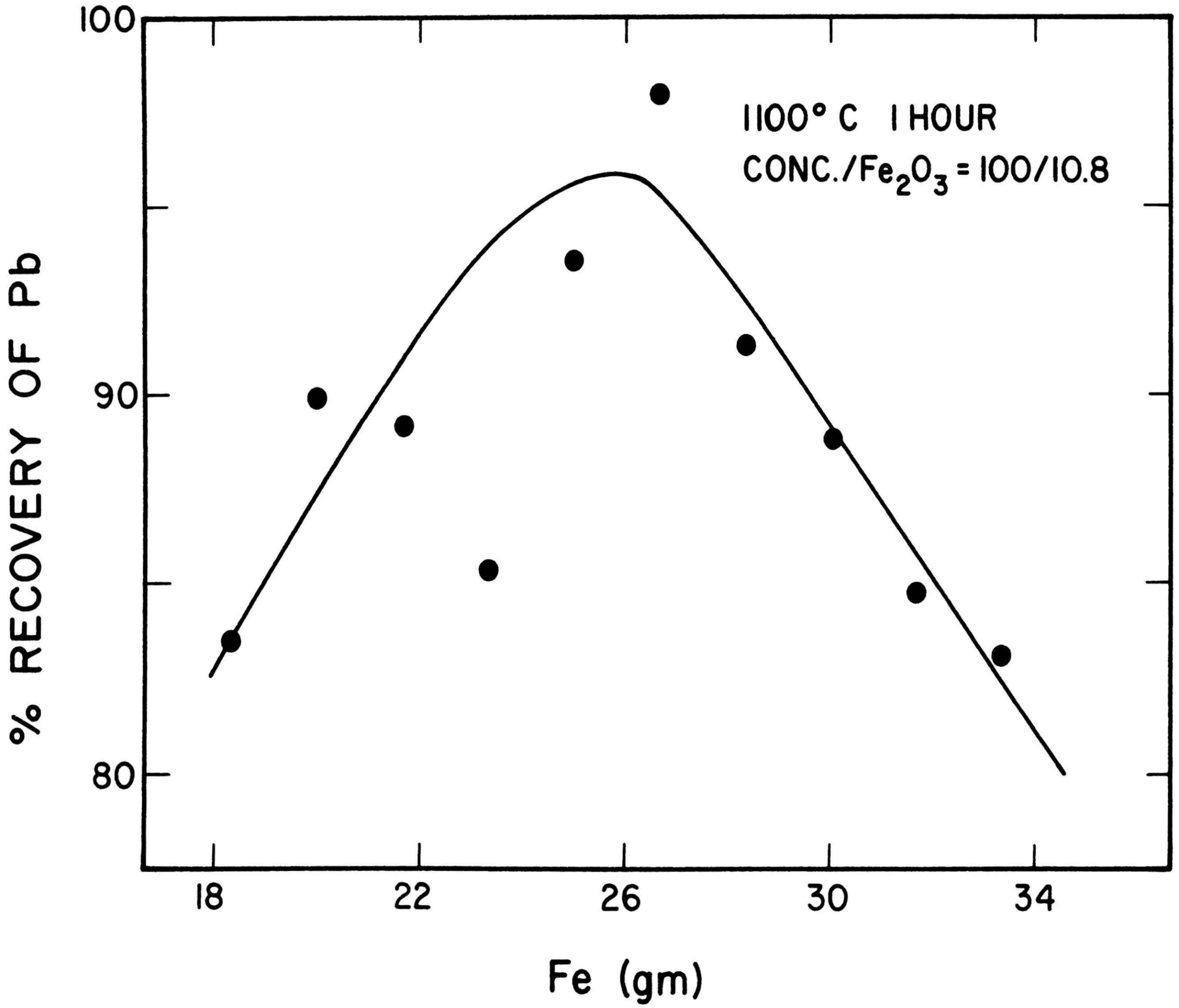

Figure 16. Recovery of Lead vs Iron with Fe_2O_3 as Flux

ratio of 100/10.8/25. The results are shown in Figure 17 (Table IXd).

The next series of experiments determined the effect of amount of iron on the lead recovery. For 1 hour runs at a concentrate/Fe_3O_4 ratio of 100/7.5, the amount of iron added varied from 18 to 30 gm. As shown in Figure 18 (Table IXe), a maximum recovery of lead occurred at about 22.5 gm. In the next series of experiments the effect of amount of Fe_3O_4 was determined. The amount of Fe_3O_4 varied from 6 to 18 gm and the results are shown in Figure 19 (Table IXf). In these tests the matte usually overflowed the iron crucible, and presumably some lead was carried out before it had a chance to settle to the bottom. In an attempt to avoid overflow, the charge was compacted into pellets of different diameters, but overflow still occurred.

Since it was observed that the matte contained many particles of metallic lead, another series of runs was carried out in which generally similar amounts of ingredients were used, except that the matte was crushed and the larger lead particles screened out through a 14 mesh screen. The lead particles that did not pass the screen were then considered in the total lead weight. The results are shown as a dotted line in Figure 19 (Table IXg).

b. Discussion

When time was varied for a sample of concentrate/Fe_3O_4/Fe of 100/10.8/25, apparently the maximum recovery is not attained in 1-3/4 hours. However, it was found later that the above ratio was not close to the optimum. When the content of iron was varied the maximum amount of reduced lead was found to occur when the iron content was 22.5 gm. After the maximum lead recovery is attained it decreases for an increased amount of iron. This may be due to many particles of lead that remained in the matte and were not weighed. Figure 19 shows that for an increased amount of Fe_3O_4 there is an initial improvement in the recovery of lead. As more flux is added to the system, more particles of lead are retained in the matte. But if the particles of lead in the matte are recovered as was done for the other series of runs shown in Figure 19, it is possible to obtain recoveries

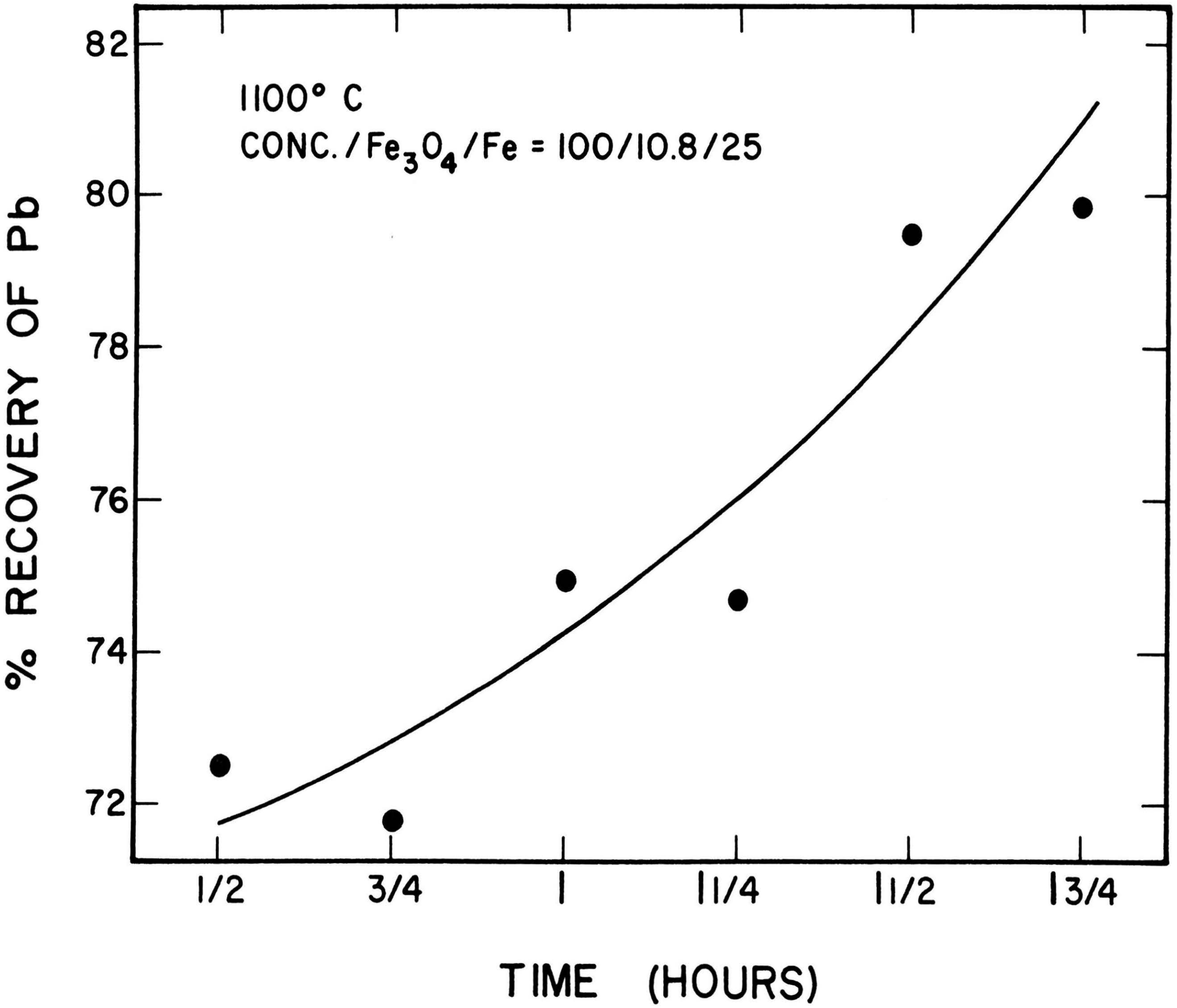

Figure 17. Comparison of Recovery of Lead at Different Times with Fe_3O_4 as Flux

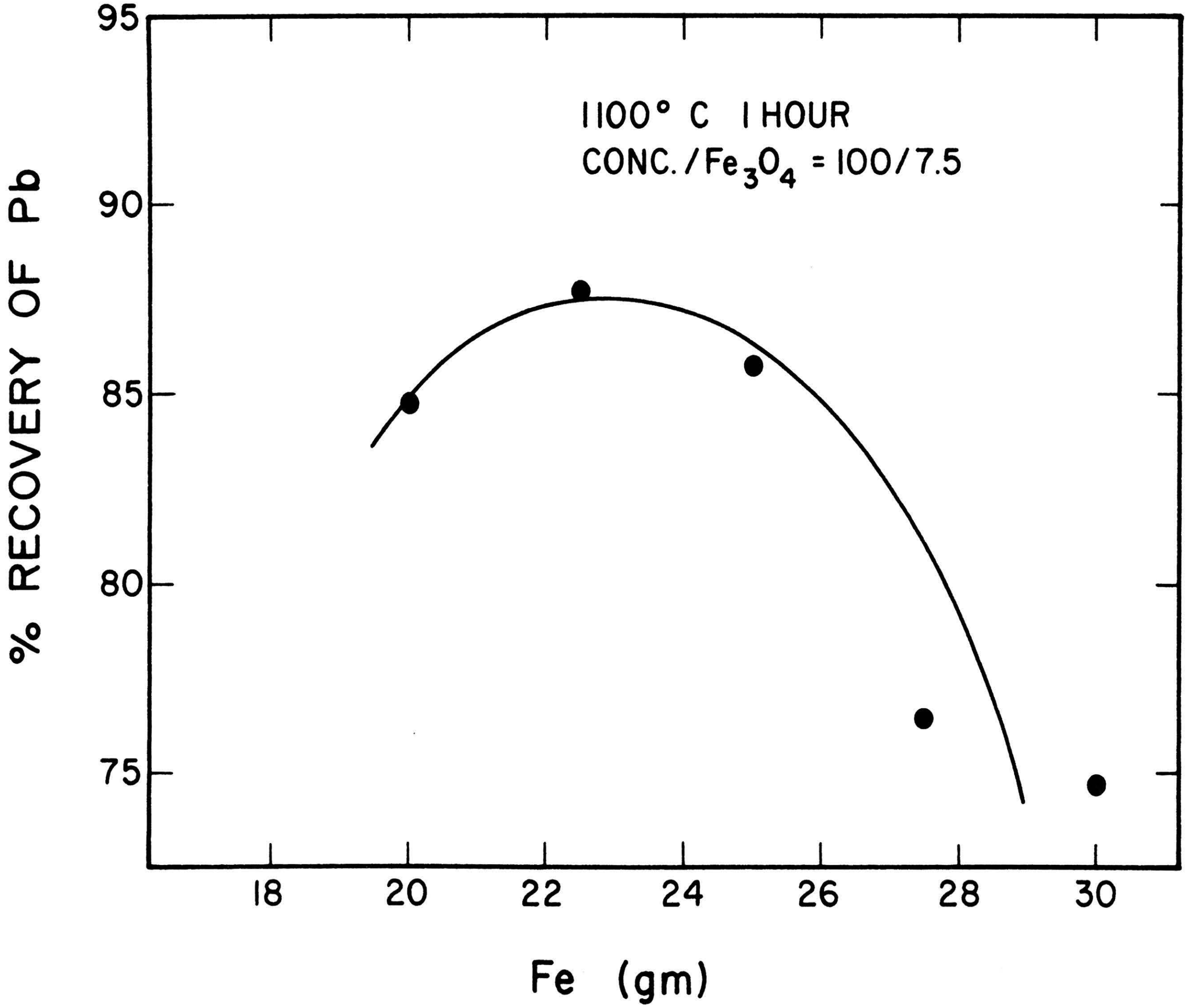

Figure 18. Recovery of Lead vs Iron with Fe_3O_4 as Flux

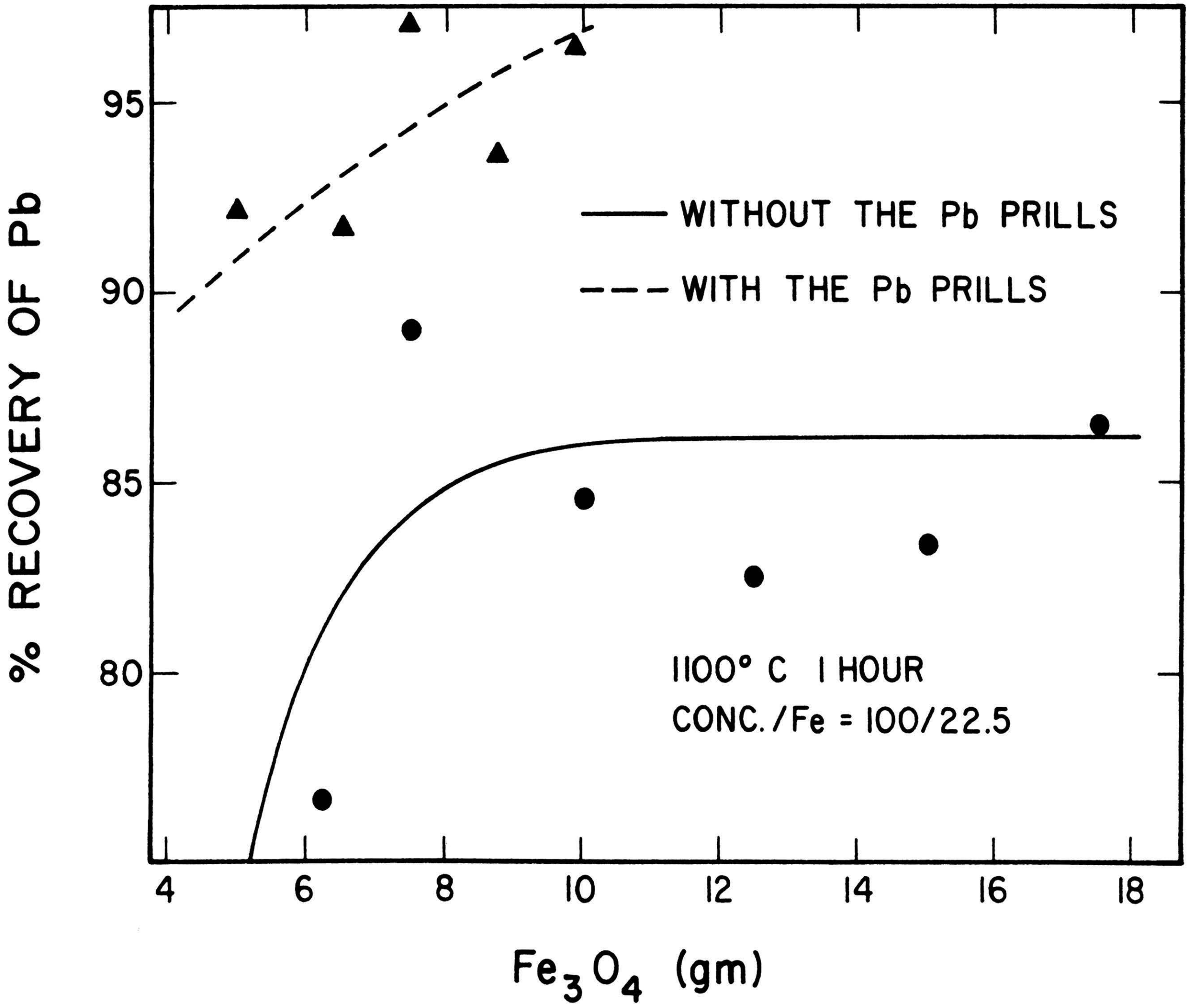

Figure 19. Recovery of Lead vs Fe_3O_4 as Flux

over 95%. The optimum proportion of concentrate/Fe_3O_4/iron is about 100/10/22.5, based on the mixtures tried.

A comparison of the fluxing behavior of Fe_2O_3 to that of Fe_3O_4 shows that the latter flux tended to give more problems with overflow during smelting, and entrapment of lead prills in the matte. However, the recovery of lead was over 95% with both fluxes, if the prills from the Fe_3O_4 tests are added to the ingot weight. For the apparent optimum ratio of concentrate/Fe_3O_4/Fe of 100/10/22.5, the matte would have a composition of 63.5% Fe, 31.0% S, and 5.5% O. For the apparent optimum of concentrate/Fe_2O_3/Fe of 100/10.8/26, the matte would have a composition of 65.5% Fe, 28.5%, S, and 6.0% O. The above matte compositions were calculated on the assumption of 100% PbS reduction, and neglecting Cu and Zn.

3. Smelting of Concentrate Using $PbSO_4$ as Flux

a. Results

The objective in investigating the effect of $PbSO_4$ as an oxygen bearing flux was to simulate automobile battery scrap material as a possible flux for the direct smelting process. The iron and oxygen were calculated from the best results obtained using Fe_2O_3 as flux, and converting to corresponding amounts of $PbSO_4$ and Fe (an exact conversion is not possible). This was equivalent to about a concentrate/$PbSO_4$/Fe ratio of 100/16/35.

The effect of amount of iron on the lead recovery at concentrate/$PbSO_4$ of 100/16 was examined first, and the results plotted in Figure 20 (Table IXh). The recovery of lead was calculated as follows: the total lead input was considered to be the sum of the lead in the concentrate plus the lead in the $PbSO_4$. The ingot weight was divided by this total input weight to get the percent recovery. No overflow was present in this set of experiments but the tendency of the matte to trap many particles of lead was still observed.

For a fixed amount of iron (35 gm), the effect of amount of $PbSO_4$ added was investigated. The range of $PbSO_4$ contents was 10 to 17 gm, and the results are shown in Figure 21 (Table IXi).

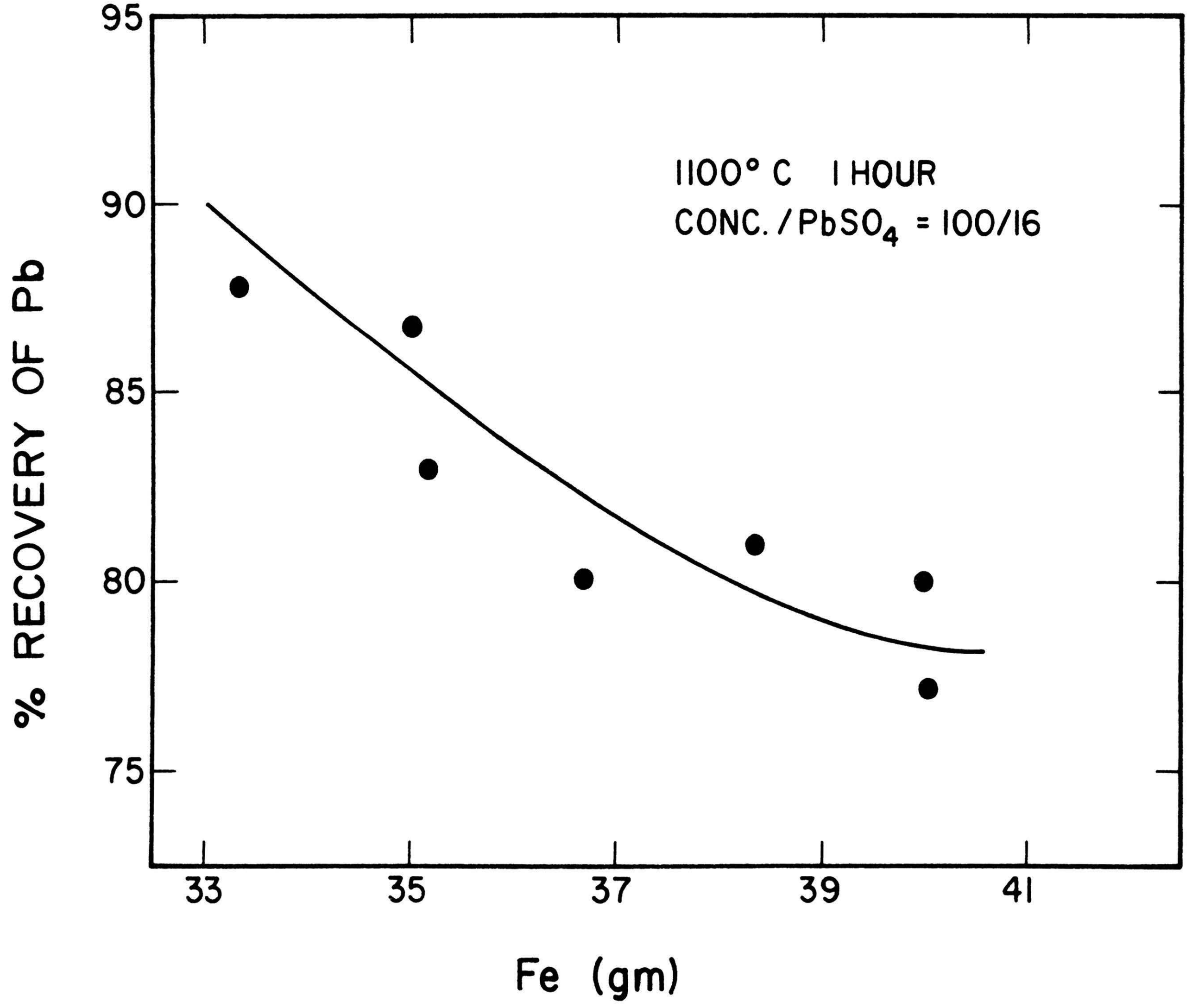

Figure 20. Recovery of Lead vs Iron with $PbSO_4$ as Flux (Including Prills)

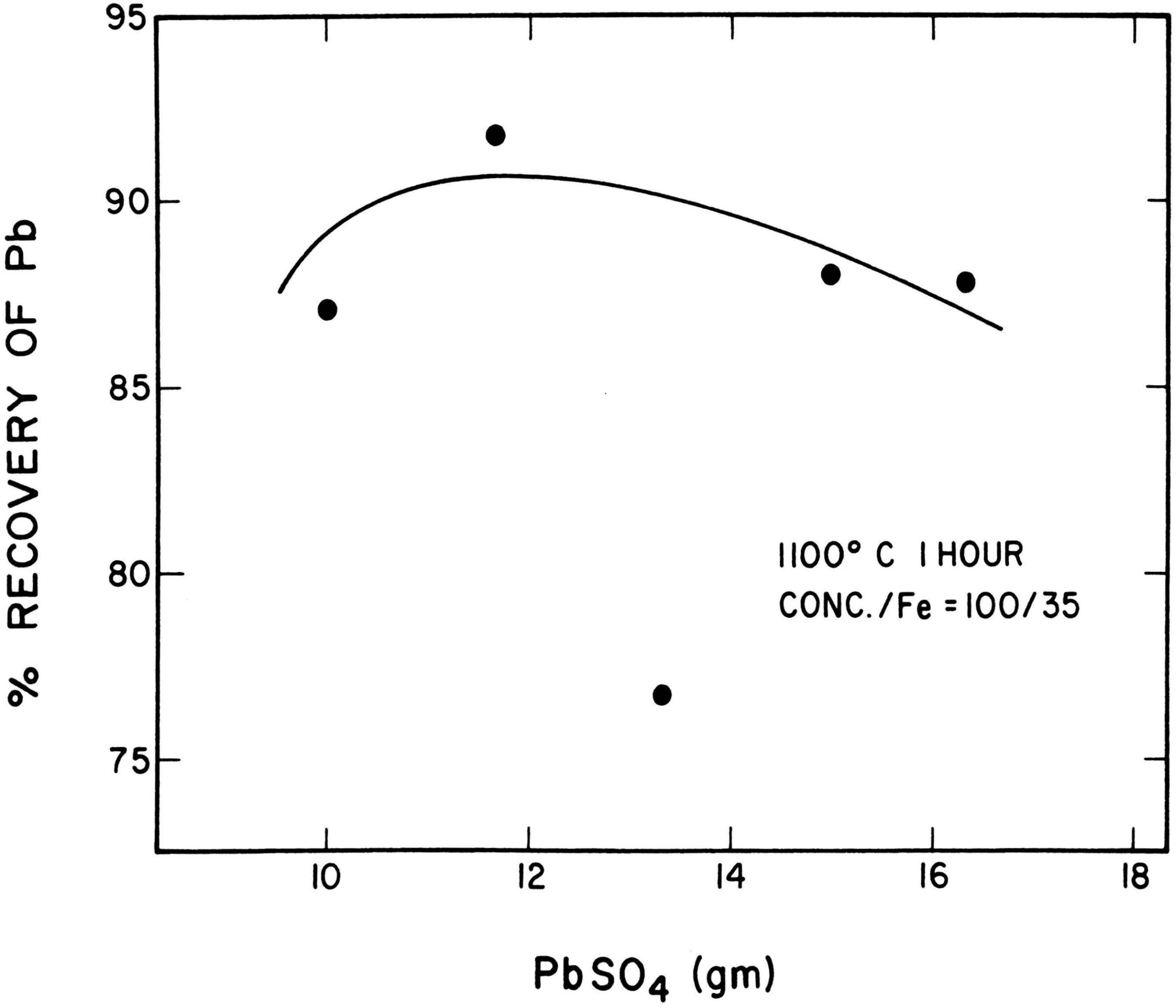

Figure 21. Recovery of Lead vs PbSO$_4$ as Flux (Including Prills)

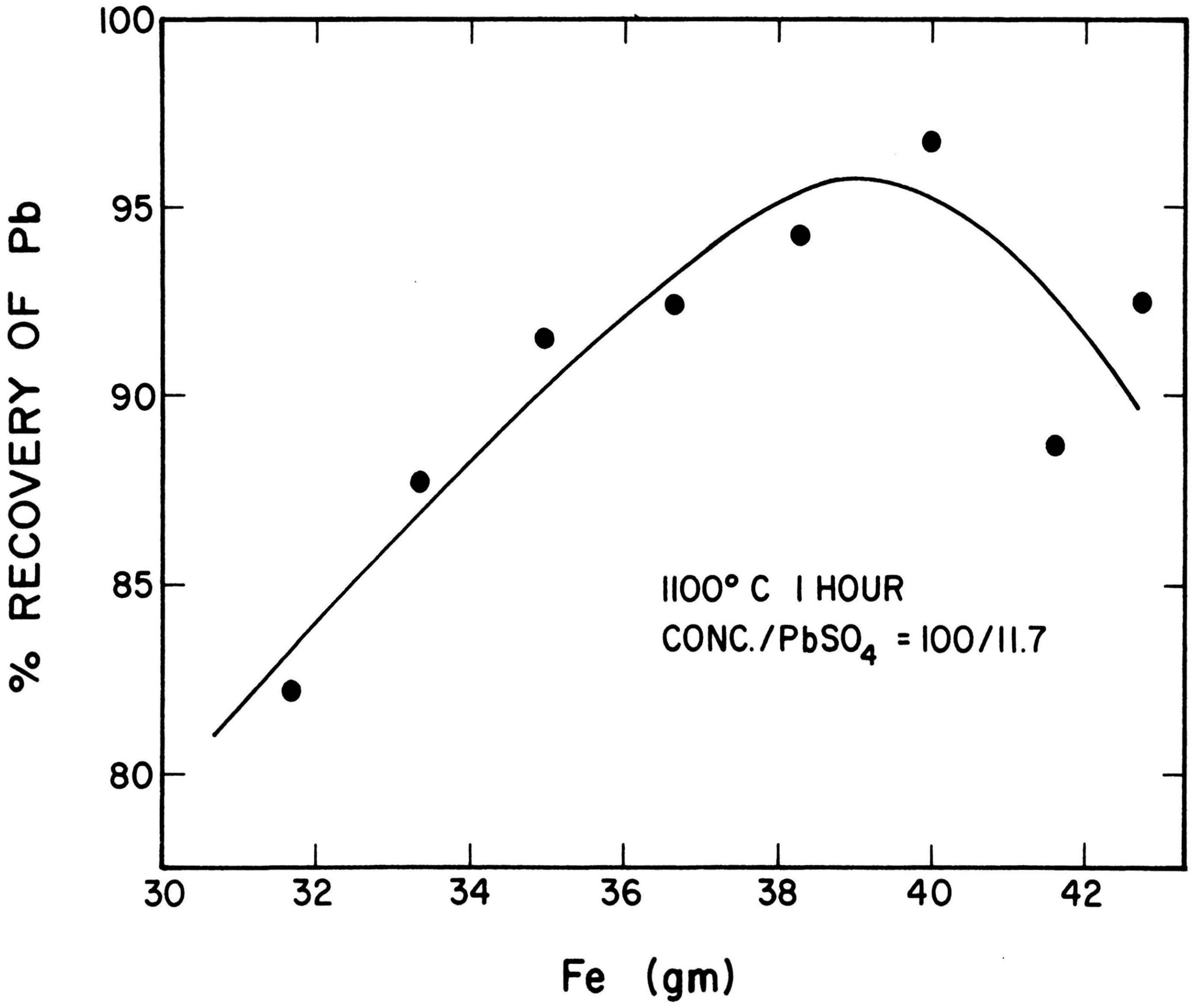

Figure 22. Recovery of Lead vs Iron with $PbSO_4$ as Flux (Including Prills)

Then once a nearly optimum amount of $PbSO_4$ was found (11.7 gm), a mixture of this ratio (concentrate/$PbSO_4$=100/11.7) was prepared. The amount of iron was varied between 31 to 43 gm, and the results are shown in Figure 22 (Table IXj). In all of the experiments using $PbSO_4$ as a flux, the particles of lead in the matte were screened out with a 14 mesh screen and counted in the total weight.

b. Discussion

Figure 20 shows that for the initial amounts of iron and flux selected for study there is no clear value for maximum recovery of lead. Figure 21 shows that the maximum recovery of lead occurs at about 12 gm of $PbSO_4$ but the trend is not well defined. In the last series of experiments using 11.7 gm of $PbSO_4$ as flux it is possible to see a more clearly defined effect of iron. The ratio of ingredients to give the best recovery of any of those tried can be seen from Figure 22. A maximum recovery of lead of about 95% is attainable for a 100/11.7/40 proportion of concentrate/$PbSO_4$/Fe. The greater consumption of iron with $PbSO_4$ as a flux, as compared to the consumption of iron when iron oxide is the flux, is caused by the additional iron that is necessary to reduce the $PbSO_4$ to metallic lead.

The matte composition for the above apparent optimum concentrate/$PbSO_4$/Fe ratio was calculated with the same assumptions used in calculating the matte composition using iron oxide as a flux. The matte contained 68.9% Fe, 27.2% S, and 3.9% O, which is somewhat higher in Fe than the matte composition found nearly optimum for iron oxide as a flux. It should be pointed out, however, that there is no way to tell if the matte contained particles of metallic iron.

Figure 23 shows the 1100°C isothermal section for the Fe-S-O system[36]. This diagram shows that iron saturated mattes contain from 69.2% to 72.5% Fe, 17.3 to 27.5% S, and 0 to 13.5% O. Only a very narrow composition range is possible in equilibrium with wustite or magnetite. The point labeled "matte composition" was calculated from chemical analysis of the phase identification sample that will be discussed later.

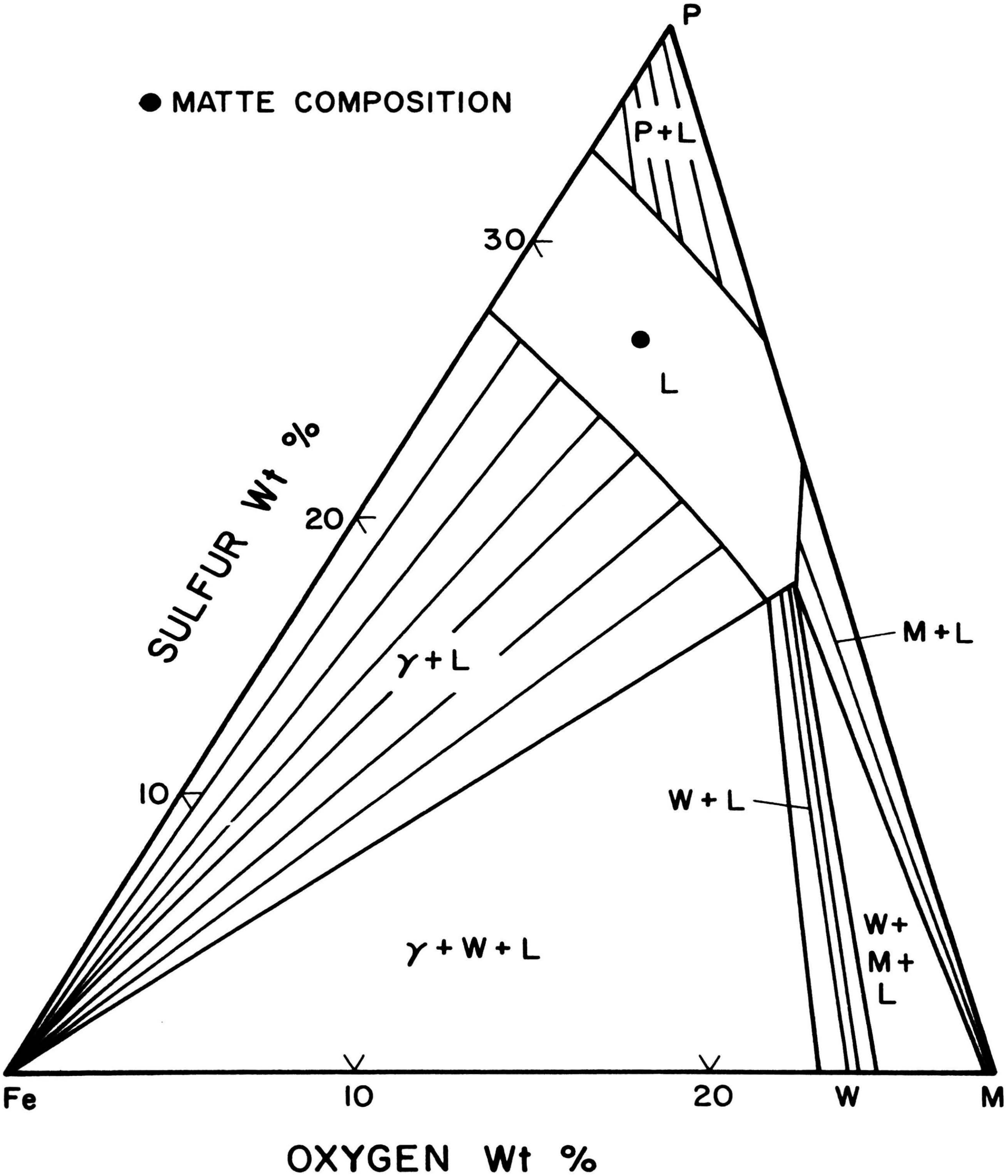

Figure 23. 1100°C Isothermal Section of the Fe-O-S System (γ=Iron, P=Pyrrhotite, W=Wustite, M=Magnetite, L=Liquid)[35]

D. The SO_2 Determination

The ratio of ingredients that gave the best lead recovery using Fe_2O_3 as flux were 100/10.8/26 of concentrate/Fe_2O_3/Fe. A mixture of this ratio was used in conducting the SO_2 determination tests. As mentioned earlier, the runs were carried out in flowing nitrogen in a tube furnace at 1100°C for 1 hour. No noticeable evolution of SO_2 occurred after about 25 minutes. The results are shown in Table II.

Table II Results of SO_2 Evolution Tests at 1100°C

Test	Volume of N_2 cc (STP)	SO_2 Concentration ppm (Volume)	Recovery of Pb %
1	300	80	93.2
2	300	70	95.5
3	300	80	92.1

The maximum SO_2 evolution allowed by some state laws is 10% of the sulfur charged. In 30 gm of concentrate there were 4.68 gm of sulfur. In 300 cc of gas, the average concentration of SO_2 was 76 ppm, which gives 0.0325 mg of sulfur evolved from the sample. This corresponds to 0.0007% of the charge sulfur evolved, and is thus a negligible SO_2 evolution compared to conventional lead smelting processes.

Several runs were made weighing the sample before and after smelting to determine the weight loss. Some of the samples overflowed the iron crucible. The results of the two successful tests are shown in Table III; the same ratio was used as for the SO_2 runs.

Table III Weight Loss of Crucible and Sample During Smelting

Test	Initial Weight gm	Final Weight gm	Weight Change gm	Recovery of Pb %
1	65.652	65.652	0.0	92.7
2	65.876	65.817	0.059	94.1

The results show that little or no weight loss occurs during the smelting reactions.

E. Phase Identification

Three different reaction products were always evident in the smelted samples: metallic lead in the bottom of the crucible, a matte in the middle, and a black porous sponge in the upper part of the crucible. These products were shown in Figure 14. The lead and the matte were molten during the run, but the black sponge appeared to have only partly melted, if at all. As mentioned earlier, the matte and black sponge usually contained some small prills of metallic lead.

The nature of the matte and black sponge were examined by X-Ray diffraction, and the results and compound identification are shown in Tables IV and V. The analysis was made on a sample with a concentrate/ Fe_2O_3/Fe of 100/10.8/26. The sample was smelted in the tube furnace for 1-1/2 hours at 1100°C and cooled over a 5 hour period.

Table IV X-Ray Diffraction Patterns for the Matte, and Assumed Compound

d Spacing Angstroms	I/I_1*	Compound	d Spacing Angstroms	I/I_1	Compound
1.72	80-100	FeS	2.49	60-80	FeO
2.08	80-100	FeS	1.24	30-60	FeS
2.16	80-100	FeO	1.42	30-60	Fe or FeS
2.67	80-100	FeS	1.45	30-60	FeS
3.07	80-100	FeS	1.47	30-60	FeS
1.52	60-80	FeO	1.49	30-60	Pb or FeS or Fe_3O_4
1.92	60-80	ZnS	1.59	30-60	FeS
1.93	60-80	FeS	2.47	30-60	Pb
1.64	60-80	ZnS	2.55	30-60	FeS or Fe_3O_4
2.04	60-80	Fe	2.89	30-60	Pb
3.15	60-80	ZnS			

* I/I_1 = Relative Intensity

Since there was a large number of lines on each pattern, some uncertainty exists regarding the identification of compounds for which only the weaker lines were present. Future work should include a more detailed X-Ray analysis of each reaction product after some sort of chemical or magnetic separation of each product into different parts. A more detailed analysis might discover small amounts of compounds not yet detected, and more definitely establish the existence of compounds giving only weak lines in the present patterns.

Table V X-Ray Diffraction Patterns for the Black Sponge, and Assumed Compound

d Spacing Angstrom	I/I_1*	Compound	d Spacing Angstrom	I/I_1*	Compound
2.85	80-100	$Ca_2MgSi_2O_7$	1.56	30-60	Ca_2MgSiO_7
2.48	80-100	$Ca_2MgSi_2O_7$	1.59	30-60	$Ca_2MgSi_2O_7$
1.39	60-80	$Ca_2MgSi_2O_7$	1.91	30-60	$Ca_2MgSi_2O_7$
1.74	60-80	$Ca_2MgSi_2O_7$	2.03	30-60	$Ca_2MgSi_2O_7$
1.76	60-80	$Ca_2MgSi_2O_7$	2.28	30-60	$Ca_2MgSi_2O_7$
1.81	60-80	$CaMgSiO_4$	2.39	30-60	$Ca_2MgSi_2O_7$
2.55	60-80	Fe_3O_4	2.94	30-60	$CaMgSiO_4$
2.57	60-80	$CaMgSiO_4$	1.63	10-30	$CaMgSiO_4$ or Fe_3O_4
2.65	60-80	$CaMgSiO_4$	3.1	10-30	$Ca_2MgSi_2O_7$
2.44	60-80	$Ca_2MgSi_2O_7$	3.5	10-30	$Ca_2MgSi_2O_7$
1.43	30-60	$Ca_2MgSi_2O_7$	3.60	10-30	$CaMgSiO_4$
1.49	30-60	Fe_3O_4	3.89	10-30	$CaMgSiO_4$
1.52	30-60	Fe_3O_4			

* I/I_1 = Relative Intensity

The lines assigned to the compound FeS were taken from A.S.T.M. Card 11-151, the lines for FeO from Card 6-0711, the lines for ZnS from Card 10-434, the lines for Fe from Card 6-0696, and the lines for Pb from Card 4-0686. The lines for $Ca_2MgSi_2O_7$ were taken from A.S.T.M. Card 10-391, the lines for $CaMgSiO_4$ from Card 11-353, and the lines for Fe_3O_4 from Card 11-614. In some cases, lines from different compounds occurred at the same d spacing, as noted in the tables.

In order to make a materials balance on the smelting process, a sample with 180 gm concentrate, 18 gm of Fe_2O_3, and 49.5 gm of Fe (concentrate/Fe_2O_3/Fe ratio of 100/10.8/26) was smelted in the tube furnace for 1-1/2 hr at 1100°C and cooled over a 5 hr period. Each phase was weighed, and analyzed for the principal elements present. The chemical analysis for each phase is shown in Table VI.

Table VI Chemical Analysis for Each Product

Element	Metal %	Matte %	Black Sponge %
Pb	99.5	8.4	8.8
Cu	0.35	1.9	0.2
Fe	0.07	58.8	21.1
Zn	0.01	2.0	2.2
S	0.08	23.9	2.5
O	+	4.26	28.47
Si	+	+	9.81
Ca	+	+	8.36
Mg	+	+	4.85

+ Not analyzed

The weight of each product and its chemical analysis was used to calculate the amount of each element present. This information was then used to construct an approximate materials balance as shown in Table VII. For Fe and S, it appears that the chemical analysis for one or the other phase was in error, or some sort of sampling error was made. Also, neither the X-Ray or chemical analysis indicates definitely whether the lead in the matte was present as metallic prills or as unreduced PbS.

In order to calculate a matte composition in terms of Fe, S, and O that could be plotted on the phase diagram for the Fe-S-O system, the following assumptions were made. First, all of the Pb in the matte was assumed to be metallic. The Cu was assumed to be Cu_2S, and the Zn to be ZnS. Then these substances were subtracted from the matte weight, and the remainder was assumed to be all Fe, S, and O. On that basis, the matte composition is 68.6% Fe, 26.2% S, and 5.0% O. The matte composition calculated above is the composition plotted as a point on Figures 4 and 23.

Table VII Mass Balance for the Smelted Material (with a Fixed Ratio of Concentrate/Fe_2O_3/Fe of 100/10.8/26)

Phase	Calculated Wt. of Elements from Chemical Analysis gm						Actual Wt. of Each Phase gm
	Pb	Cu	Zn	Fe	S	0	
Sponge	0.8	0.0	0.2	1.9	0.2	2.6	9.2
Matte	9.1	2.1	2.2	63.2	25.8	4.6	107.7
Lead	123.0	0.4	0.0	0.1	0.1		123.6
Total	132.9	2.5	2.4	65.2	26.1	7.2	240.50*
Wt. Loss or (gain)	0.6	0.6	0.7	(1.5)	(1.9)	0.7	

* About 7.8 gm lost during removal of sample from crucible

VI. SUMMARY AND CONCLUSIONS

The results of the investigation demonstrate that metallic iron is a very effective reducing agent for lead from a typical Missouri lead concentrate, if the proper amounts of flux are added. If the sample contained the optimum ratio of concentrate/flux/Fe, the recovery was repeatedly over 95% for 1 hr at 1100°C. The results also show that the evolution of SO_2 from the sample during smelting is extremely low. The products of reaction consist of metallic lead, an oxysulfide matte, and a partly fused black porous spongy material, which might be called a slag. On cooling, the matte consists primarily of a mixture of FeS and FeO. The matte also contains most of the Zn and Cu originally present in the concentrate. The sponge consists mainly of calcium magnesium silicates and magnetite. Only the lead and the matte appeared to be completely molten at 1100°C.

Thermochemical calculations indicate that the matte composition with the lowest sulfur pressure should give the least unreduced PbS in the matte. Such a matte would be in equilibrium with both metallic iron and wustite (univariant "c" on Figure 7), and would have about 18% S and 13% O. The results show, however, that the matte composition actually found to give the greatest % Pb recovery contained about 4% O and 26% S (depending on which procedure was used to calculate the matte composition). Further work is needed to determine why mattes with higher oxygen contents did not give high recoveries of lead.

The results show that a variety of oxygen-bearing fluxes can be used for the process, all of which gave Pb recoveries greater than 96%. In preliminary experiments, steel making furnace flue dusts worked very well, and in the present work, simulated lead battery scrap also worked well.

X-Ray examination of the slow-cooled matte showed that it tends to segregate into different compounds. This gives hope that the matte may be recycled to the mill for recovery of the copper and zinc values, as well as extraction of any unreduced galena. Investigation of such a matte treatment is also a good topic for future work. In addition, work needs to be done to find out which phase contains the precious metals present in the concentrate.

The present work has established that the direct reduction of a lead concentrate is readily achieved under the proper conditions, while at the same time emitting no significant amounts of objectionable gases. Much work remains to be done, however, before the process can be investigated profitably on a pilot plant scale. A better understanding of the thermochemistry of the process is needed, together with thermal requirements, rates of reactions, and truly optimum matte composition for maximum recovery. In addition, methods of recovering the other valuable metals from the matte should be investigated. The present work provides an excellent starting point for planning such future work.

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VITA

Rolando O. Fernandez was born in Oruro Bolivia (Latin America), on July 8, 1945. He received basic education in his hometown, and a Bachelor of Science degree in Metallurgical Engineering from the Technical University of Oruro in 1969.

He was research assistant at the Research Institute of Mining and Metallurgy of Bolivia (a United Nations program), and a teaching assistant at his former university.

He entered the graduate school of the University of Missouri-Rolla in January 1972. He has been a student member of the Metallurgical Society of AIME, and member of the International Platform Association.

APPENDICES

APPENDIX A
SUMMARY OF PRELIMINARY WORK

The results of the preliminary experiments are presented on the following tables. These experiments were performed by various students of the Metallurgical Department of UMR. In order to have a general look at the reduction of lead concentrates by metallic iron and different fluxes, a variety of crucible materials, sample weights, times, and temperatures were used. The concentrate used in these preliminary experiments contained 75.0% Pb.

Table VIIIa Recovery of Lead for a Fixed Ratio of Concentrate/Fe of 100/25.2 at 1200°C for 35 Minutes using Fireclay Crucibles and No Flux

Test	Weight Conc. gm	Weight Fe gm	Weight Pb gm	Recovery (%)
1	250.0	63.0	102.3	54.6
2	250.0	63.0	135.7	72.4
3	250.0	63.0	105.1	56.0
4	250.0	63.0	--	--
5	202.1	51.4	64.0	42.3
6	203.2	51.4	82.0	53.8
7	203.5	51.5	84.0	54.9
8	167.7	42.3	73.0	58.1

Table VIIIb Recovery of Lead for Variable Ratios of Concentrate/Fe_2O_3/Fe at 1200°C for 35 Minutes using Fireclay Crucibles

Test	Weight Conc. gm	Weight Fe gm	Weight Fe_2O_3 gm	Weight Pb gm	Recovery Pb %
1	159.8	40.2	10.0	97.5	81.3
2	159.8	40.2	20.0	81.0	67.5
3	166.7	33.3	10.0	91.5	73.2
4	160.0	40.0	10.0	100.0	84.4
5	151.5	48.5	10.0	98.1	86.4
6	161.3	38.7	10.0	98.8	82.3
7	156.3	43.7	10.0	104.0	89.0
8	147.2	52.8	10.0	92.5	83.7
9	160.0	44.8	8.0	92.3	76.7
10	160.0	44.8	12.0	96.3	80.3
11	160.0	51.2	8.0	88.5	78.3
12	160.0	40.0	10.0	101.3	84.5
13	160.0	45.0	10.0	104.3	87.0
14	160.0	50.0	10.0	104.3	87.0

Table VIIIc Recovery of Lead Concentrate using BOF Flue Dust as a Flux at 1200°C for 1/2 Hour, 60 Grams Concentrate, Porcelain Crucible

Test	Weight Fe gm	Weight Flue Dust gm	Weight Pb gm	Recovery Pb %
1	10.0	13.0	27.4	60.9
2	10.0	15.0	27.5	61.2
3	10.0	17.0	25.9	57.5
4	15.0	3.0	38.0	84.4
5	15.0	5.0	38.0	84.4
6	15.0	7.0	39.2	87.1
7	15.0	11.0	40.2	89.3
8	15.0	13.0	40.2	89.3
9	20.0	3.0	39.2	87.1
10	20.0	5.0	40.1	89.2
11	20.0	7.0	40.8	90.6
12	20.0	11.0	41.3	91.8
13	20.0	13.0	41.7	92.6
14	20.0	15.0	41.6	92.1
15	20.0	17.0	42.1	93.6
16	20.0	19.0	42.0	93.4
17	20.0	21.0	41.7	92.5
18	25.0	5.0	33.1	73.4
19	25.0	9.0	37.6	83.6
20	25.0	13.0	31.8	71.7
21	25.0	15.0	34.2	76.7

Table VIIId Recovery of Lead Concentrate using Fe_3O_4 and SiO_2 as Flux at 1050°C for 45 Minutes, Iron Crucible and Concentrate/Fe Ratio of 100/30 for the First Three Experiments and 100/28.9 for the Rest

Test	Weight Fe_3O_4 gm	Weight SiO_2 gm	Weight Pb gm	Recovery Pb %
1	4.0	--	18.6	82.4
2	6.0	--	16.6	73.8
3	4.0	--	25.7	77.0
4	5.0	--	22.6	67.0
5	6.0	--	21.6	64.0
6	7.0	--	21.2	62.8
7	3.0	1.0	21.3	63.1
8	3.0	2.0	23.7	70.6
9	4.0	1.0	21.8	64.6
10	4.0	2.0	23.2	68.9

APPENDIX B

EXPERIMENTAL RESULTS FOR LEAD SMELTING EXPERIMENTS

This Appendix presents the data obtained in the experimental work on the direct smelting of lead. Figures in the recovery of lead column were used to plot the graphs in the text. The weight of lead includes the drops of lead that were in the upper part of the crucible.

Table IXa Recovery of Lead at Different Temperatures and Times using Fe_2O_3 as Flux with a 40 gm Concentrate, 3 gm Fe_2O_3 and 11 gm of Iron, Corresponding to a Ratio of Concentrate/Fe_2O_3/Fe of 100/7.5/27.5

Test	Time hours	Temp. °C	Weight gm	Recovery %
1	1/2	1000	7.1	24.0
2	3/4	1000	8.7	29.4
3	1	1000	8.3	27.9
4	1-1/2	1000	9.1	30.5
5	1/2	1050	22.6	76.2
6	3/4	1050	23.4	78.9
7	1	1050	24.6	83.0
8	1-1/2	1050	23.0	77.6
9	1/2	1100	26.8	90.8
10	3/4	1100	28.4	95.6
11	1	1100	28.2	95.2
12	1-1/2	1100	28.6	96.3

Table IXb Recovery of Lead vs Fe_2O_3 as Flux, for a Fixed Ratio of Concentrate/Fe of 100/27.5 at 1100°C for 1 Hour with 60 gm of Concentrate, and 16.5 gm of Iron

Test	Weight Fe_2O_3 gm	Weight Pb gm	Recovery Pb %
1	2.0	38.9	87.6
2	2.5	36.0	81.0
3	3.0	37.8	85.5
4	3.5	38.9	87.6
5	4.0	39.1	87.8
6	4.5	40.2	90.4
7	5.0	42.4	95.4
8	5.5	42.4	95.4
9	6.0	43.6	98.1
10	6.5	43.3	97.1

Table IXc Recovery of Lead vs Iron using Fe_2O_3 as Flux for a Fixed Ratio of Concentrate/Fe_2O_3 of 100/10.8 at 1100°C for 1 Hour with 60 gm of Concentrate and 6.5 gm of Fe_2O_3

Test	Weight Fe gm	Weight Pb gm	Recovery Pb %
1	11.0	37.2	83.7
2	12.0	39.8	90.0
3	13.0	39.6	89.1
4	14.0	38.0	85.5
5	15.0	41.6	93.7
6	16.0	43.7	98.1
7	17.0	40.6	91.4
8	18.0	39.4	88.7
9	19.0	37.7	84.8
10	20.0	35.9	80.8

Table IXd Recovery of Lead vs Time using Fe_3O_4 as Flux for a Fixed Proportion of Concentrate/Fe_3O_4/Fe of 100/10.8/25 at 1100°C for 1 Hour with 40 gm of Concentrate and 10 gm of Powdered Iron

Test	Time hours	Weight Pb	Recovery Pb %
1	1/2	21.1	71.3
2	3/4	20.9	70.5
3	1	22.2	74.9
4	1-1/4	22.1	74.7
5	1-1/2	23.6	79.6
6	1-3/4	23.6	79.6

Table IXe Recovery of Lead vs Iron using Fe_3O_4 as Flux for a Fixed Ratio of Concentrate/Fe_3O_4 of 100/7.5 at 1100°C for 1 Hour with 40 gm of Concentrate and 3 gm of Fe_3O_4

Test	Weight Fe gm	Weight Pb gm	Recovery Pb %
1	8.0	25.0	84.6
2	9.0	26.1	87.7
3	10.0	25.4	85.7
4	11.0	22.6	76.5
5	12.0	21.7	73.4
6	13.0	24.7	83.4

Table IXf Recovery of Lead vs Fe_3O_4 as Flux using a Fixed Ratio of Concentrate/Fe of 100/22.5 at 1100°C for 1 Hour with 40 gm of Concentrate and 9 gm of Iron

Test	Weight Fe_3O_4 gm	Weight Pb gm	Recovery Pb %
1	3.0	26.5	89.2
2	4.0	25.1	84.6
3	5.0	24.6	82.7
4	6.0	24.8	83.4
5	7.0	25.6	86.5

Table IXg Recovery of Lead vs Fe_3O_4 using a Fixed Ratio of Concentrate/Fe of 100/22.5 at 1100°C for 1 Hour with 30 gm of Concentrate and 6.75 gm of Powdered Iron

Test	Weight Fe_3O_4 gm	Weight* Pb gm	Recovery Pb %
1	1.50	20.5	92.2
2	1.87	20.5	92.2
3	2.25	21.6	97.3
4	2.62	20.8	93.5
5	2.99	21.4	96.5

*Lead weight includes Pb prills

Table IXh Recovery of Lead vs Iron using $PbSO_4$ as Flux for a Fixed Ratio of Concentrate/$PbSO_4$ of 100/16 at 1100°C for 1 Hour with 30 gm of Concentrate and 4.8 gm of $PbSO_4$

Test	Weight Fe gm	Weight* Pb gm	Recovery Pb %
1	10.0	19.5	87.8
2	10.5	19.3	86.9
3	10.7	18.5	83.0
4	11.0	17.8	80.1
5	11.5	18.0	81.0
6	12.0	17.8	80.1

*Lead weight includes Pb prills.

Table IXi Recovery of Lead vs $PbSO_4$ as Flux for a Fixed Ratio of Concentrate/Fe of 100/35 at 1100°C for 1 Hour with 30 gm of Concentrate and 10 gm of Iron

Test	Weight $PbSO_4$ gm	Weight* Pb gm	Recovery Pb %
1	4.8	19.5	87.6
2	4.5	19.4	87.5
3	4.0	17.0	76.6
4	3.5	20.4	91.8
5	3.0	19.3	87.0

*Lead weight includes the Pb prills.

Table IXj Recovery of Lead vs Iron using $PbSO_4$ as Flux for a Fixed Ratio of Concentrate/$PbSO_4$ of 100/11.7 at 1100°C for 1 Hour with 30 gm of Concentrate and 3.5 gm of $PbSO_4$

Test	Weight Fe gm	Weight* Pb gm	Recovery Pb %
1	9.5	18.6	83.6
2	10.0	19.5	87.8
3	10.5	20.4	91.5
4	11.0	20.6	92.4
5	11.5	21.0	94.3
6	12.0	21.6	96.7
7	12.5	19.8	88.9
8	13.0	20.6	92.5

*Lead weight includes the Pb prills.

APPENDIX C

HYPOTHETICAL PHASE DIAGRAM FOR THE Fe-Pb-S AND Fe-Pb-S-O SYSTEM

One way in which to visualize how the fluxing of FeS might act to increase lead reduction from a matte is to construct a hypothetical phase diagram for the Fe-Pb-S system. Then, a modification of the diagram can be proposed to show the effect of added oxygen. The diagram must be hypothetical, since no data exist to construct the actual diagram.

A possible isothermal diagram for the Fe-Pb-S system at 1100°C is shown in Figure 24. Only that part of the system of interest to the present work is sketched in the Figure. The diagram shows a liquid matte region extending from the Fe-FeS join into the ternary Fe-Pb-S system. In the absence of oxygen, the liquid matte boundary is shown as line a-b-c-d. If the addition of oxygen to the Fe-Pb-S system is assumed to decrease the solubility of PbS (and Pb) in the matte, the oxygen-containing matte might have the shape shown by the region a'-b'-c'-d'. This latter region is actually a projection of the oxygen-containing section (system Fe-Pb-S-O) down into the Fe-Pb-S section.

Point c' is the composition of the oxygen-containing matte in equilibrium with both metallic iron and lead. It has a lower Pb and PbS content than point c, which is also in equilibrium with both iron and lead. Of course, it is possible that oxygen does not have much effect on the size of the liquid matte region. In that case, the effect of oxygen on lead recovery might be due to such factors as decreased viscosity or surface tension, which could permit better separation of the matte and reduced lead. The effect of oxygen on the shape of the liquid matte region is clearly a desirable subject for future research.

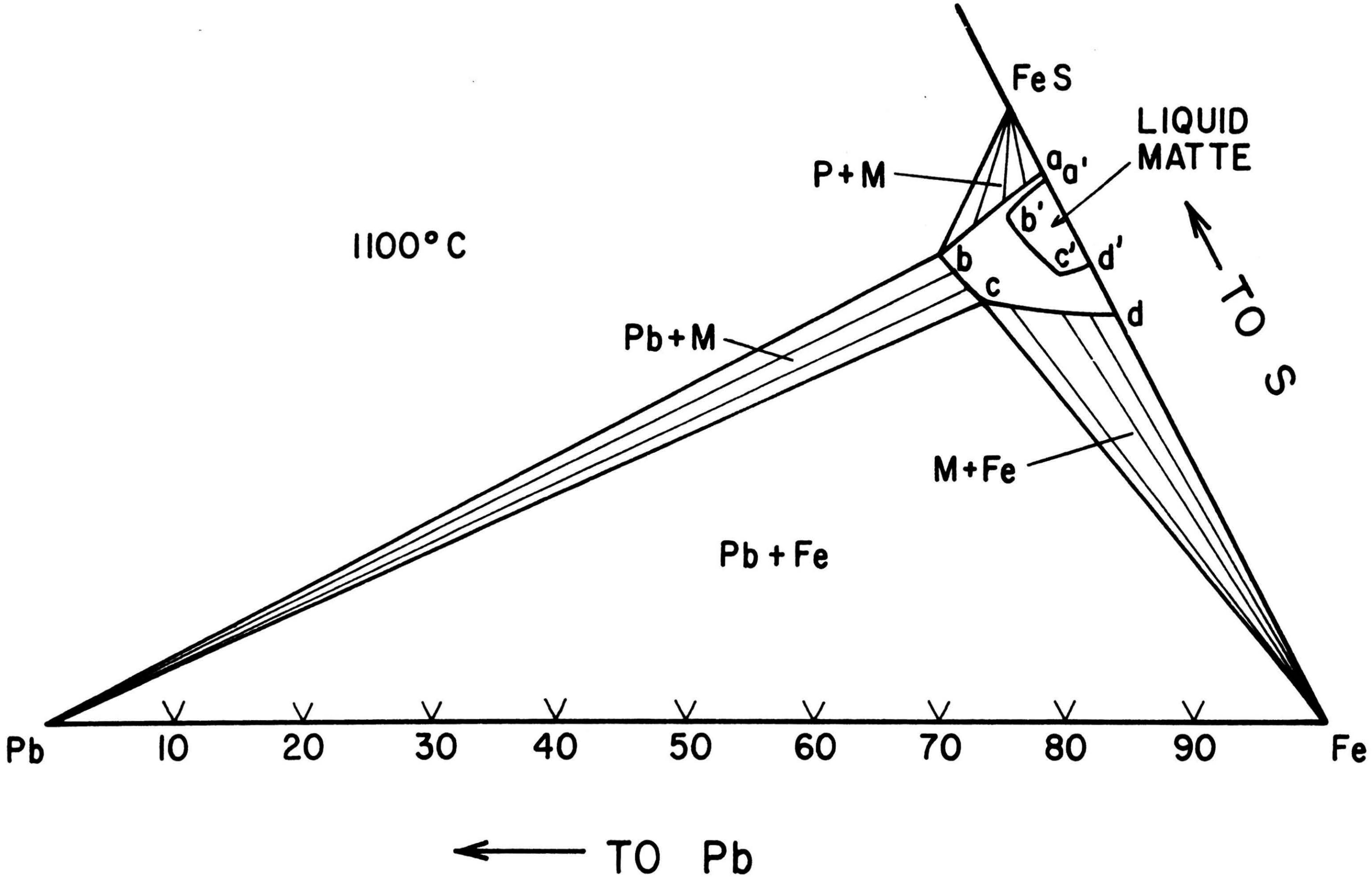

Figure 24. Hypothetical Fe-Pb-S and Fe-Pb-S-O System (Pb=Liquid Lead, Fe=Iron, M=Liquid Matte, P=Pyrrhotite)