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# Solubility of Lead and Distribution of Minor Elements Between Bullion and Calcium Ferrite Slag at 1,250° C

By G. T. Fisher II and K. O. Bennington

UNITED STATES DEPARTMENT OF THE INTERIOR



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**UNITED STATES DEPARTMENT OF THE INTERIOR  
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### UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	L	liter
cm	centimeter	mL	milliliter
cm <sup>3</sup>	cubic centimeter	mL/min	milliliter per minute
°C	degree Celsius	mm	millimeter
g	gram	min	minute
h	hour	pct	percent
in	inch	wt pct	weight percent

# SOLUBILITY OF LEAD AND DISTRIBUTION OF MINOR ELEMENTS BETWEEN BULLION AND CALCIUM FERRITE SLAG AT 1,250° C

By G. T. Fisher II<sup>1</sup> and K. O. Bennington<sup>2</sup>

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## ABSTRACT

The U.S. Bureau of Mines conducted research on calcium ferrite slags to determine the distribution of Pb and minor elements (Ag, Cd, Zn, and Co) between Pb bullion and slag. These fundamental data are required to evaluate nonferrous smelting with calcium ferrite slags as a substitute for conventional iron silicate slags. Determinations were made in 25-cm<sup>3</sup>-capacity MgO crucibles at 1,250° C for 2 h in a CO-CO<sub>2</sub> atmosphere with an O<sub>2</sub> potential that would retard the formation of magnetite. Calcium ferrite slag composition variables studied were from 16 to 32 wt pct CaO in 2-pct increments and SiO<sub>2</sub> ranging from 1 to 5 wt pct in 1-pct increments with equal additions of MgO. For all compositions studied, the retention of Pb in the calcium ferrite slag was less than 1 wt pct, which compares favorably to about 6 wt pct Pb in conventional iron silicate slags used in smelting of Pb concentrates. Minor element distribution was insensitive to changes in slag composition in the range studied. However, slag composition had significant impact on the melting and fluidity of the slag.

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## INTRODUCTION

Autogeneous or direct smelting of Pb and Cu concentrates is an important recent development in the field of nonferrous extractive metallurgy. In the case of Pb, direct smelting offers several potential advantages over blast furnace smelting, according to Matyas (1):<sup>3</sup> elimination of the sintering operation, with its high circulating load of return sinter; elimination of the need for coke; reduction of the fuel requirement owing to the utilization of the exothermic heat of oxidation reactions for smelting; potential for the use of pure O<sub>2</sub> instead of O<sub>2</sub>-enriched air; and production of a gas substantially richer in SO<sub>2</sub> than obtainable with sintering. The problems to be solved in the direct smelting process include considerable loss of Pb to slag and dust, and a high-PbO slag must be produced to obtain a low-S bullion, necessitating a slag-cleaning step. The emerging direct Pb smelting processes, such as Boliden's Kaldo, Kivcet, Outokumpo flash, and Queneau-Schuhmann-Lurgi (QSL), require two stages to combine production of a low-S bullion with a high-Pb recovery.

Iron silicate slags traditionally have been used as the mainstay for nonferrous smelting, including blast furnace operations; however, calcium ferrite slags offer distinct advantages (2-5). Preliminary data (2) indicate that dissolution of Pb in the ferrite slag is approximately an order of magnitude lower than that in the iron silicate type slag. The ferrite slag alternative has a lower melting point, higher fluidity, higher PbO activity coefficient, lower FeO activity, and greater density, which may permit production of a low-S bullion and a low-Pb slag. All of these characteristics make the calcium ferrite slag more suitable than the iron silicate slag for direct smelting.

The thermodynamics of calcium ferrite slags recently have been investigated at nonferrous smelting temperatures (2). Oxygen isobars and liquidus isotherms in the CaO-FeO-Fe<sub>2</sub>O<sub>3</sub> system were determined at 1,200° and 1,300° C. The effects of O<sub>2</sub> potential, temperature, and CaO content were related to the oxidation state of Fe, Fe<sup>+3</sup>-Fe<sup>+2</sup> ratio. A study of the equilibrium between liquid Pb and slag as a function of O<sub>2</sub> potential ( $1 \times 10^{-12}$  to  $1 \times 10^{-8}$  atm) were studied and showed that the solubility

of Pb in the slag [log (weight percent Pb in slag)] increased linearly with increasing O<sub>2</sub> potential and was less by approximately a factor of 10 than in the iron silicate slag. Distributions of Pb between dust, slag, and bullion were calculated at 1,200° C for a 0.3-wt pct S content in bullion for high- and common-grade Pb concentrates in a feasibility study (4). The energy requirement for the single-step Pb smelting process was calculated using process fuel equivalent. Results indicated that the recovery of Pb as bullion with low S could be greatly improved by use of the calcium ferrite slag. Process fuel equivalent for the single-step process was one-third of the conventional blast furnace process, and compared favorably with the QSL and Kivcet processes. Recently, laboratory-scale experiments were performed to produce Pb bullion by injecting PbS reagent or concentrate and O<sub>2</sub> gas onto a slag layer (5). The Pb content of the produced calcium ferrite slag was low, being at most 5 wt pct, at a S content in the bullion of 2 wt pct. In comparison, the dissolution of Pb in iron silicate slag was extremely high, amounting to about 50 pct at the same S content in the bullion. Increasing O<sub>2</sub> content in the O<sub>2</sub>-N<sub>2</sub> input gas decreased Pb loss as chemical dust, resulting in a high recovery of Pb as bullion.

Data on the retention of Pb in the bullion-ferrite slag system have been confined to slags containing 25 wt pct CaO (4-5). No data on the effects of silica and magnesia have been reported in the open literature. The distribution of minor elements among the phases encountered in Pb smelting is important because it is desirable to retain valuable elements, such as Ag, present in the bullion phase. Studies of the distribution of minor elements in the Pb bullion-ferrite slag system also have not been found in the open literature.

In the present investigation, the U.S. Bureau of Mines determined the effects of slag composition, including the CaO flux content and presence of SiO<sub>2</sub> and MgO, on the retention of Pb in the slag and the distribution of minor elements in the Pb bullion-calcium ferrite slag system. Minor elements used in this study were Ag, Cd, Co, and Zn.

## EXPERIMENTAL PROCEDURES

The effects of calcium ferrite slag composition and the distribution of minor elements Ag, Cd, Co, and Zn, between the slag and bullion were obtained by heating

prefused master slags, oxide additions, Pb, and minor elements in 25-cm<sup>3</sup> MgO crucibles under controlled CO-CO<sub>2</sub> atmospheres in a vertical SiC resistance-heated tube furnace at 1,250° C for 2 h and O<sub>2</sub> potential of  $1 \times 10^{-10}$  atm. Procedures were matched to other experimental work in the CaO-FeO-Fe<sub>2</sub>O<sub>3</sub> phase diagram (6), with the

<sup>3</sup>Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

1,250° C melting contour being parallel and within the reported 1,200° and 1,300° C contours. Trial determinations from 1/2 to 4 h were made, with 2 h being an apparent optimum for melting and equilibrium. After the required time at temperature, the sample was quickly lowered out of the hot zone and quenched in a water-jacketed Cu container with Ar atmosphere. Bullion and slag were separated and analyzed.

## EXPERIMENTAL DESIGN

A series of experiments was conducted in which Pb and minor elements were placed in the bottom of the crucible and slag constituents were added on top.

The charge consisted of 5 g of Pb; 25 g of prefused master slag; and SiO<sub>2</sub>, MgO, Ag, Cd, Zn, and Co as needed. Additional CaO powder was added to adjust for the increase in slag weight by SiO<sub>2</sub> and MgO additions. Also, for compositions with CaO contents greater than 24 wt pct, the 24-pct-CaO master slag was used, and CaO was added to attain the desired composition. All constituents were weighed on an analytical balance to 0.0001 g. Calcium oxide contents in the slags were varied from 16 to 32 wt pct in increments of 2 wt pct. Additions of SiO<sub>2</sub> ranged from 1 to 5 wt pct in increments of 1 wt pct with equal addition of MgO. Minor elements investigated were held at 3 wt pct of the Pb charge for Ag, Zn, and Cd, and 0.3 wt pct of the Pb charge for Co, constituting 0.15 and 0.015 g, respectively.

## CRUCIBLE AND MASTER SLAG PREPARATION

Since MgO crucibles were unavailable commercially, the Bureau prepared its own. The crucibles were prepared by slip casting in plaster molds. A 1,000-g batch of MgO powder was mixed for 30 h with 450 mL of ethyl alcohol in a 4.5-L porcelain mill with 3/4-in-diam alumina balls. A slurry of 36 g calcium carbonate and 50 mL ethyl alcohol was prepared and mixed with the MgO slurry prior to slip casting. The green slip-cast crucibles were allowed to air dry for 1 to 2 days, then fired in a muffle furnace at 1,550° C for 24 h in air, and allowed to furnace cool. The 25-mL crucibles were approximately 1.75 in high, with a 1-in top diameter and .075-in-thick wall.

Batches of synthetic master slags (1,900 g) were prepared from commercially obtained CaO, Fe, and Fe<sub>2</sub>O<sub>3</sub> powders. Slags were prepared containing 16 to 24 wt pct CaO in increments of 2 wt pct. Iron oxide-to-iron weight ratio in the initial mixture was held constant at 4.297:1 to provide an Fe<sub>2</sub>O<sub>3</sub>-to-Fe mole ratio of 1.5. Powders were mixed and packed into ZrO<sub>2</sub> crucibles, covered with a graphite plate, and heated in an electrically heated furnace to a temperature between 1,150° and 1,250° C within 6 h, held at the desired temperature for 1 h, and allowed to

furnace cool. The crucible was removed by chipping and grinding, and the slag was subsequently ground to minus 50 mesh.

## APPARATUS

A diagram of the inner furnace apparatus for equilibrating slag and bullion is shown in figure 1. The vertical SiC resistance tube furnace (50 mm ID) maintained the sample at 1,250° C ± 2° C over a height of 80 mm using a Radiamatic<sup>4</sup> sensor head connected to a controller. A Pt versus Pt-10 pct Rh thermocouple measured the temperature of the furnace 25 mm above the sample. The furnace assembly permitted the introduction of the sample into the constant temperature zone after the system was flushed with Ar. The CO-CO<sub>2</sub> gas mixture was obtained from gas cylinders and dried by passing the gases through columns packed with Drierite (anhydrous CaSO<sub>4</sub>). Gas flows of CO and CO<sub>2</sub> were controlled by the use of constant pressure-head capillary flowmeters with Department of Transportation (DOT3) brake fluid as both manometer and pressure-head fluid. The gas mixture was calculated to give an O<sub>2</sub> potential of 1 x 10<sup>-10</sup> atm at 1,250° C using gas flows of 165 mL/min CO and 235 mL/min CO<sub>2</sub>. The gases passed through columns of Drierite, then to a mixer, and were introduced within approximately 3 cm of the top of the furnace assembly via a 5-mm-ID alumina (Al<sub>2</sub>O<sub>3</sub>) tube that was approximately 60 cm above the sample to provide a uniform and reproducible atmosphere. The sample was held for 2 h at 1,250° C and then was rapidly lowered into a water-jacketed Cu container fitted at the bottom of the furnace, and quenched in an Ar atmosphere.

## ANALYTICAL METHODS

The Pb bullion was analyzed for Ag, Ca, Cd, Co, and Zn by pressure dissolution in a dilute nitric-fluoboric acid solution and analyzed by conventional flame atomic absorption spectrophotometry. Slags obtained were analyzed for Ag, CaO, Cd, Co, MgO, Pb, SiO<sub>2</sub>, Zn. MgO and Pb analysis samples were prepared by dissolving the sample in an open dish with a nitric-perchloric-hydrofluoric acid solution and analyzed by flame atomic absorption spectrophotometry. Samples for Ag, Cd, Co, and Zn were dissolved in a nitric-perchloric acid solution and analyzed by flame atomic absorption spectrophotometry. SiO<sub>2</sub> analyses were accomplished by a gravimetric method by sulfuric acid dehydration. Calcium oxide analysis was done by a wet volumetric method in a hydrochloric-nitric acid solution by potassium permanganate titration.

<sup>4</sup>Reference to specific manufacturers does not imply endorsement by the U.S. Bureau of Mines.

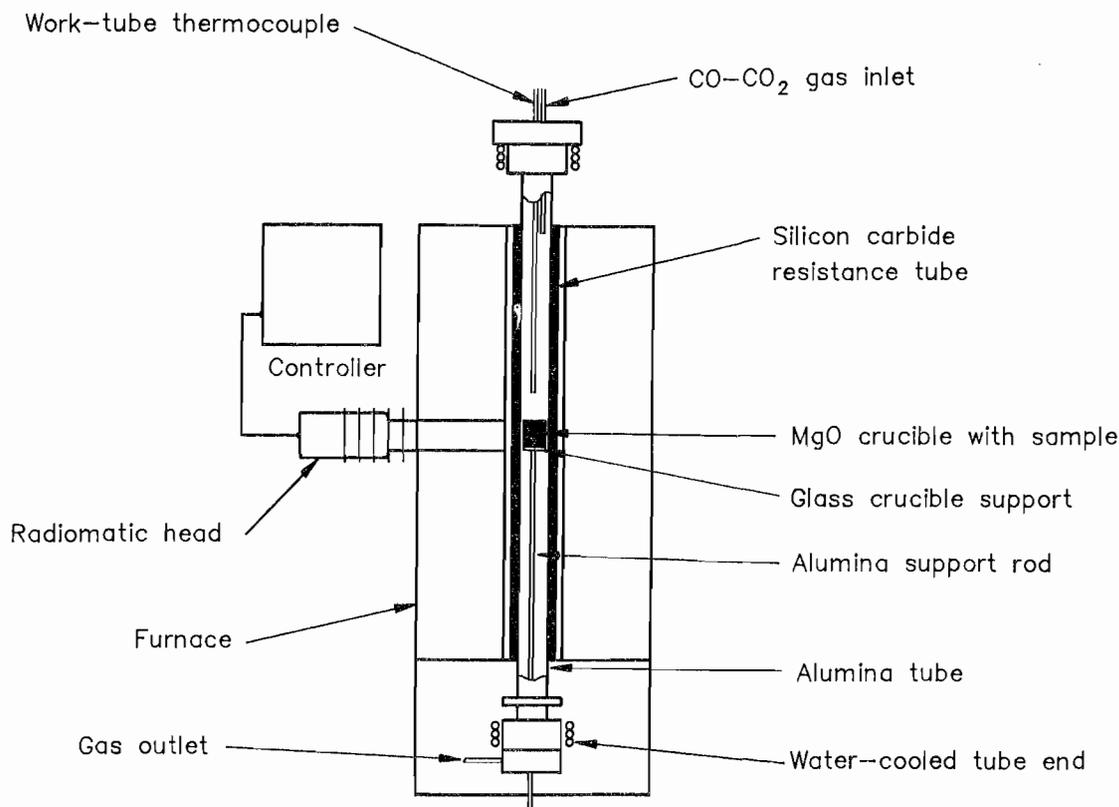


Figure 1.—Experimental furnace apparatus.

## RESULTS AND DISCUSSION

The retention of Pb in the ferrite slag and distribution of minor elements Ag, Cd, Co, and Zn were determined for slags containing 16 to 32 wt pct CaO and 1 to 5 wt pct SiO<sub>2</sub> with equal additions of MgO. For these determinations, the Pb and minor elements were placed on the bottom of the crucible, and the slag constituents were added on top. A summary of the chemical analyses of the bullion and slag samples for these elements is given in the appendix. Mass balance calculations were performed using the slag and bullion chemical analyses to calculate losses of these elements to volatilization, the percentage of the retained minor elements reporting to the Pb bullion, and the percentage of the retained Pb reporting to the slag. For these calculations it was assumed that—

1. Weight of the slag equals weight of prepared master slag plus weight of added CaO plus weight of SiO<sub>2</sub> plus weight of MgO.
2. Weight of Pb bullion equals total initial weight of sample minus calculated weight of slag minus measured weight loss of sample.

The calculated loss of Pb and minor elements is summarized in table 1. The calculated percentage of the

retained Pb reporting to the slag and the percentages of minor elements reporting to the Pb bullion are summarized in table 2. Results of the investigation showed that the slag composition did not have a significant effect on the retention of Pb into the slag and the percentage of minor elements reporting to the bullion phase. However, slag composition had a pronounced effect on the melting-nonmelting boundary. Metallographic samples of slags were prepared to search for evidence and criteria to interpret melting; however, these metallographic observations did not contribute to the identification of melting because many slags disintegrated and well-sintered slags could not always be distinguished from those that were melted. The melting boundary zone was inferred (fig. 2), because a definitive method to distinguish between melting and sintering was not identified. The factors used in determining this inferred boundary were size and distribution of vugs and metallic beads, material wetting or shrinking away from the crucible walls, and appearance of the slag. Fluidity of the slag is critically important in decreasing the bullion retention by the slag, and experimental conditions were chosen to take advantage of this fact.

Table 1.—Summary of losses of Pb, Co, Cd, Zn, and Ag from mass balance calculations,<sup>1</sup> percent

Run	Pb	Co	Cd	Zn	Ag	Run	Pb	Co	Cd	Zn	Ag
16-2-1 ...	-1.3	31.1	93.6	38.2	-2.0	24-10-2 ..	8.9	26.7	94.8	67.2	13.6
16-2-2 ...	5.4	-35.8	93.6	33.0	.2	26-2-1 ...	-5.4	45.3	78.2	38.6	-.1
16-4-1 ...	2.1	-9.9	99.2	2.4	14.2	26-2-2 ...	-6.2	12.7	85.1	33.1	19.7
16-4-2 ...	3.2	44.3	98.4	31.9	13.3	26-4 .....	-6.8	71.9	99.3	60.4	13.7
16-6 .....	1.5	-11.4	98.8	38.2	7.0	26-6-1 ...	-3.1	-15.6	78.6	32.4	26.5
16-8 .....	7.5	47.2	99.3	92.4	15.9	26-6-2 ...	-6.6	82.3	95.9	83.1	12.5
16-10 .....	13.9	37.9	99.3	87.2	8.6	26-8 .....	3.4	76.5	95.6	64.6	12.9
18-2 .....	-10.1	-27.0	89.1	33.6	5.0	28-2-1 ...	-2.3	33.0	94.2	50.0	6.3
18-4-1 ...	4.1	-44.5	98.6	25.9	10.6	28-2-2 ...	-4.7	27.5	76.5	42.3	15.0
18-4-2 ...	.1	-28.4	90.7	14.1	-5.3	28-4 .....	2.8	24.3	98.3	49.3	10.0
18-6 .....	3.1	20.8	98.6	60.5	12.9	28-6-1 ...	-.5	-38.1	79.4	28.3	11.6
18-8 .....	6.1	16.4	98.8	78.1	20.6	28-6-2 ...	-7.2	23.6	98.6	38.4	13.1
20-2 .....	-1.7	29.8	93.0	47.3	-.2	28-6-3 ...	-6.6	35.9	83.7	35.9	15.2
20-4 .....	-.8	-21.7	91.0	37.8	18.9	28-8 .....	3.1	47.0	90.9	43.7	18.2
20-6-1 ...	-7.0	43.2	94.0	42.0	11.5	30-2-1 ...	-4.7	39.9	77.1	41.8	3.2
20-6-2 ...	-.7	38.2	99.1	47.5	34.4	30-2-2 ...	-5.7	41.9	81.1	42.8	11.5
20-8 .....	2.8	58.2	93.5	86.7	13.9	30-4 .....	-4.9	21.1	96.4	33.5	10.9
22-4 .....	1.4	43.6	98.1	4.1	9.7	30-6-1 ...	-3.9	-12.3	87.6	19.8	19.3
22-6-1 ...	11.4	73.5	97.1	61.4	12.7	30-6-2 ...	2.3	26.5	94.8	61.9	18.9
22-6-2 ...	2.4	20.4	92.2	57.0	13.4	30-8-1 ...	3.1	-30.8	85.7	29.0	15.3
22-8-1 ...	3.0	40.0	90.7	55.1	12.4	30-8-2 ...	-6.7	38.7	88.6	38.9	24.6
22-8-2 ...	1.1	63.0	99.7	69.7	11.6	32-2 .....	-3.4	40.2	81.7	42.7	10.1
22-10 ...	6.3	30.8	99.1	53.1	17.1	32-4 .....	-5.1	-13.2	98.2	5.1	10.6
24-4 .....	-3.2	29.8	96.8	50.0	9.9	32-6-1 ...	-6.7	65.4	98.9	62.8	13.4
24-6 .....	.3	38.2	96.4	57.3	9.3	32-6-2 ...	1.8	50.5	83.5	39.1	36.1
24-8 .....	-1.8	62.2	98.7	59.3	8.8	32-8-1 ...	-7.5	55.7	94.8	85.0	31.5
24-10-1 ..	5.7	51.2	98.9	53.4	18.4	32-8-2 ...	-3.3	71.6	97.5	65.9	15.5

<sup>1</sup>Negative numbers indicate a calculated weight gain.

<sup>2</sup>First and second numbers indicate weight percent, respectively, of CaO and SiO<sub>2</sub> + MgO in slag. Third number, if any, indicates multiple tests.

Table 2.—Summary of retained minor elements reporting to bullion and of Pb reporting to ferrite slag, percent

Run	Co	Cd	Zn	Ag	Pb	Run	Co	Cd	Zn	Ag	Pb
16-2-1 ...	1.90	72.70	1.10	98.30	4.60	24-10-2 ..	10.20	82.70	9.50	98.70	0.80
16-2-2 ...	.90	82.70	.90	92.90	3.50	26-2-1 ...	1.30	92.20	.50	96.70	1.60
16-4-1 ...	2.90	29.40	1.00	99.10	2.70	26-2-2 ...	.78	89.70	.42	97.90	2.60
16-4-2 ...	2.80	63.70	.94	97.80	3.50	26-4 .....	2.50	75.50	.18	99.80	.36
16-6 .....	2.00	21.50	1.60	99.20	3.60	26-6-1 ...	1.40	85.63	.90	98.43	2.77
16-8 .....	24.20	9.60	46.80	99.50	.50	26-6-2 ...	5.78	91.00	1.93	99.59	.21
16-10 .....	33.40	12.50	65.00	99.50	.30	26-8 .....	5.03	90.51	.93	99.52	.48
18-2 .....	.80	83.70	.50	99.20	3.80	28-2-1 ...	.52	81.30	.34	96.90	1.68
18-4-1 ...	1.30	7.10	1.30	99.40	1.40	28-2-2 ...	1.90	94.90	.93	99.40	1.00
18-4-2 ...	.25	60.40	.19	98.30	4.50	28-4 .....	1.26	88.43	.71	99.56	.78
18-6 .....	4.10	6.80	8.20	98.90	2.00	28-6-1 ...	.70	90.40	.90	99.30	1.20
18-8 .....	7.40	5.10	8.70	99.50	.80	28-6-2 ...	1.43	31.75	.89	99.14	.68
20-2 .....	.96	85.40	.45	98.30	2.70	28-6-3 ...	4.42	94.27	1.70	99.56	.56
20-4 .....	.50	88.20	.16	99.30	1.20	28-8 .....	6.07	88.17	1.81	99.47	.42
20-6-1 ...	4.30	88.40	1.30	99.60	.70	30-2-1 ...	5.30	93.70	.25	98.00	2.20
20-6-2 ...	16.52	78.08	5.20	99.71	.48	30-2-2 ...	1.80	92.40	.67	97.80	2.20
20-8 .....	7.70	87.60	10.00	99.50	.27	30-4 .....	1.32	84.27	1.02	99.58	.74
22-4 .....	2.90	70.70	.70	98.60	1.70	30-6-1 ...	.90	83.95	.88	99.76	.79
22-6-1 ...	5.66	85.56	.62	99.27	1.17	30-6-2 ...	2.21	76.05	.87	98.20	.40
22-6-2 ...	3.30	90.00	1.50	99.60	1.10	30-8-1 ...	1.50	87.70	1.80	99.20	.90
22-8-1 ...	5.20	89.20	1.50	99.30	.90	30-8-2 ...	17.21	91.16	3.57	99.73	.34
22-8-2 ...	3.59	25.11	.77	99.78	.51	32-2 .....	2.30	94.90	.98	99.20	.90
22-10 ...	17.60	3.70	17.70	96.80	1.20	32-4 .....	.92	78.04	.41	99.57	.94
24-4 .....	.99	88.89	.56	99.61	.80	32-6-1 ...	3.07	62.82	1.85	99.31	.27
24-6 .....	1.56	89.44	.55	98.74	1.34	32-6-2 ...	4.05	86.94	1.47	98.32	.32
24-8 .....	7.94	84.67	1.86	99.79	.36	32-8-1 ...	6.37	54.03	4.11	99.70	.50
24-10-1 ..	13.20	60.40	4.60	99.20	.40	32-8-2 ...	3.48	82.92	.83	99.75	.26

<sup>1</sup>First and second numbers indicate weight percent, respectively, of CaO and SiO<sub>2</sub> + MgO in slag. Third number, if any, indicates multiple tests.

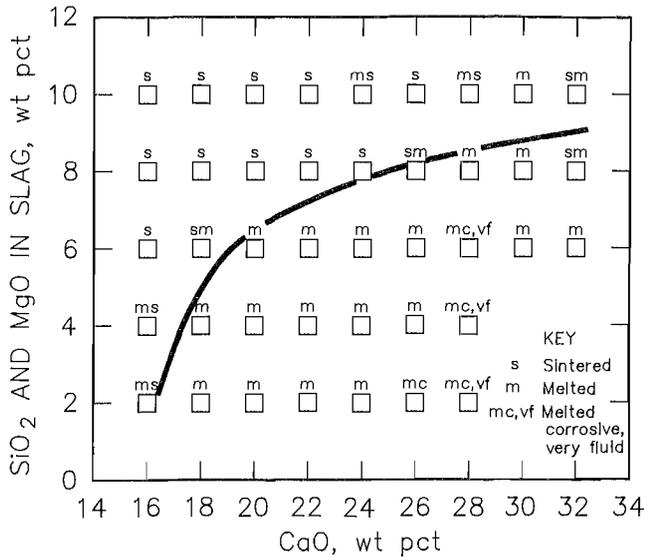


Figure 2.—Inferred melting boundary between sintered and melted slag compositions.

The solubility of Pb in the ferrite slags is summarized in table 3, and shown as a function of slag composition in figure 3. The Pb content of the slags appears to decrease with increasing CaO and SiO<sub>2</sub>, plus MgO in the slag. The analyzed Pb content in the slags was less than 1 wt pct, and a mean value for the data was 0.238 wt pct. This value corresponds to 1.3 pct of the Pb reporting to the slag. In all cases, the Pb solubility in the ferrite slags is quite low in comparison with the dissolution of Pb in iron silicate slags, which are reported to be about 6 wt pct under similar conditions (2). Calculated mass balance results are summarized in table 1. Lead is not a volatile constituent in the system, thus any losses can be in analytical uncertainty. Reported Pb gains at 5 pct or above are a result of no weight loss data available (taken to be 0) and thus overestimate the weight of the bullion. Weight of the bullion for mass balance calculations consider volatilization of Zn and Cd, but not actual amounts of minor elements and Pb retained in the slag, since slag and bullion could not be effectively separated and weighed accurately. Bullion and slag weights for mass balance were calculated under aforementioned assumptions. Also, Pb analyses of the bullion were not made, thus are calculated from minor element analyses of the bullion.

Data on the percentage of Ag reporting to the bullion show that on the average, 98.9 pct of the Ag reports to the bullion phase, as summarized in table 2 and shown in figure 44. The distribution of Ag between bullion and slag phases appears to be independent of slag composition. Mass balance calculations in table 1 indicate loss of Ag

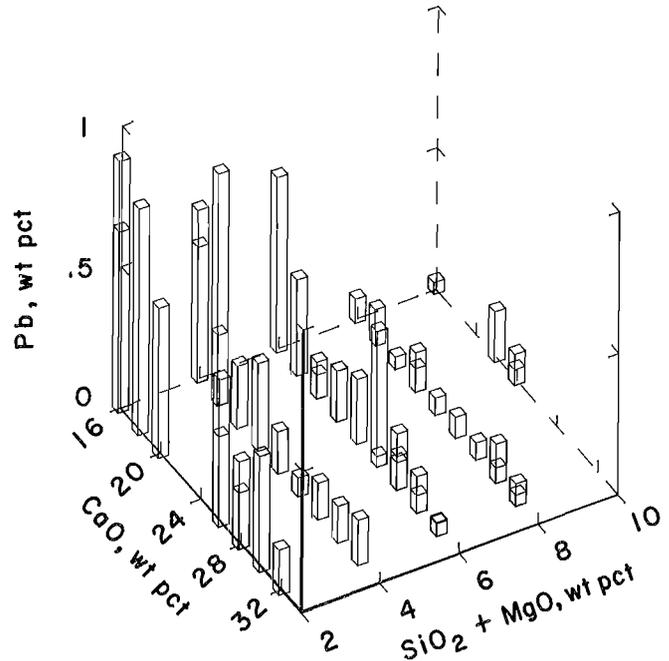


Figure 3.—Effect of ferrite slag composition on solubility of Pb in slag.

between 5 to 20 pct, which reflects on the uncertainty in Ag analyses of the bullion. Average bullion analyses were 2.58 wt pct. Ag would also not be volatile in the system, thus Ag losses reflect primarily on analytical uncertainty in bullion analyses. A 0.3 wt pct difference in Ag analyses in the bullion would yield a calculated 15 pct loss in Ag.

Table 3.—Summary of chemical analyses of Pb solubility in calcium ferrite slags, weight percent

Run	Pb in slag	Run	Pb in slag	Run	Pb in slag
16-2-1 ..	.890	22-6-1 ..	.0180	28-4 ....	.0130
16-2-2 ..	.640	22-6-2 ..	.180	28-6-1 ...	.200
16-4-1 ..	.480	22-8-1 ..	.140	28-6-2 ...	.120
16-4-2 ..	.610	22-8-2 ..	.084	28-6-3 ...	.098
16-6 ....	.620	22-10 ...	.180	28-8 ....	.064
16-8 ....	.086	24-4 ....	.150	30-2-1 ...	.410
16-10 ...	.042	24-6 ....	.230	30-2-2 ...	.410
18-2 ....	.800	24-8 ....	.061	30-4 ....	.130
18-4-1 ..	.250	24-10-1 .	.056	30-6-1 ...	.130
18-4-2 ..	.820	24-10-2 .	.110	30-6-2 ...	.063
18-6 ....	.340	26-2-1 ..	.320	30-8-1 ...	.140
18-8 ....	.130	26-2-2 ..	.520	30-8-2 ...	.055
20-2 ....	.530	26-4 ....	.067	32-2 ....	.160
20-4 ....	.220	26-6-1 ..	.480	32-4 ....	.160
20-6-1 ..	.130	26-6-2 ..	.038	32-6-1 ...	.045
20-6-2 ..	.085	26-8 ....	.075	32-6-2 ...	.049
20-8 ....	.044	28-2-1 ..	.310	32-8-1 ...	.080
22-4 ....	.310	28-2-2 ..	.200	32-8-2 ...	.040

<sup>1</sup>First and second numbers indicate weight percent, respectively, of CaO and SiO<sub>2</sub> + MgO in slag. Third number, if any, indicates multiple tests.

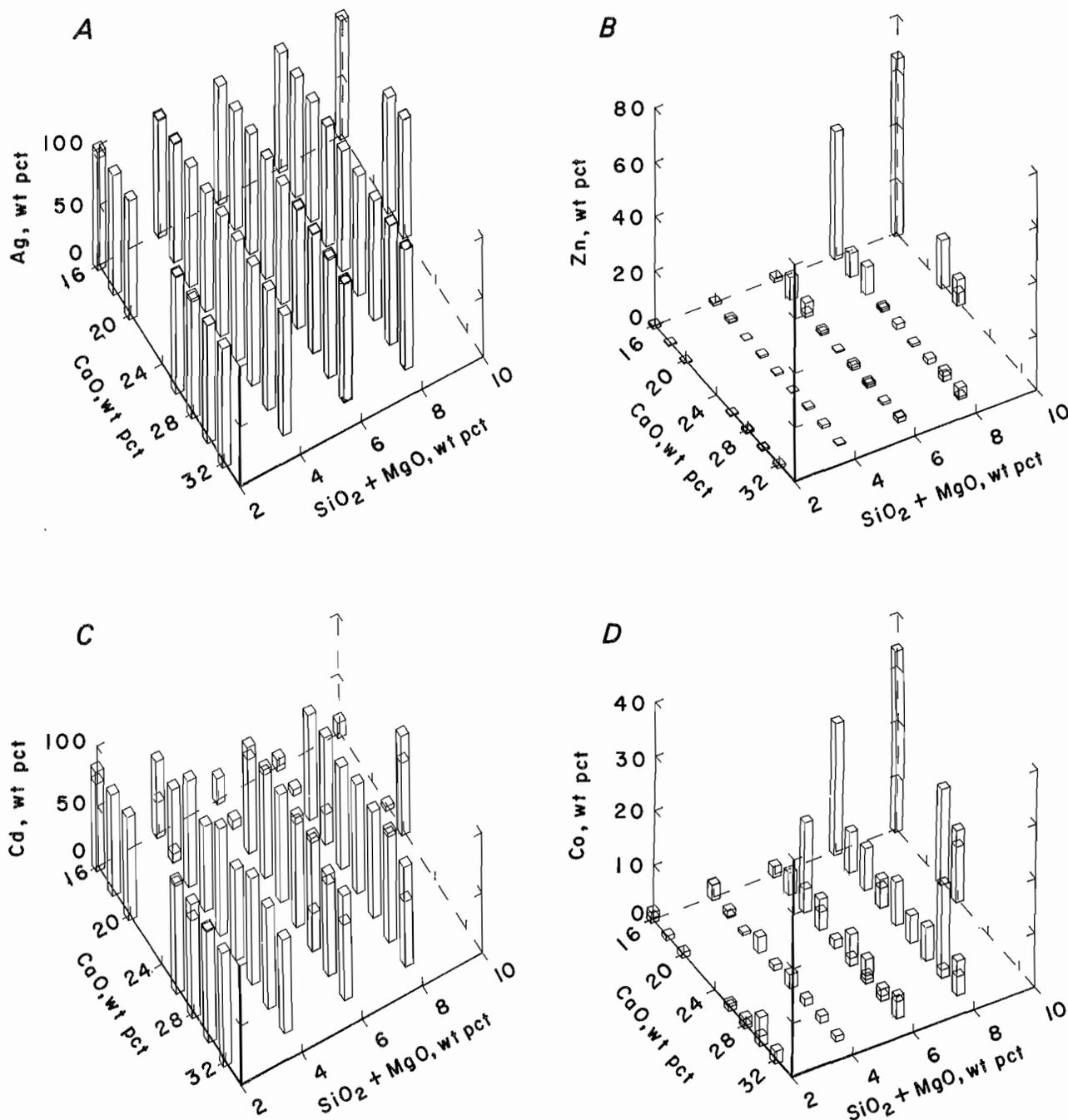


Figure 4.—Effect of ferrite slag compositions on percentage of retained minor elements reporting to Pb bullion. A, Ag; B, Zn; C, Cd; D, Co.

Calculated Zn loss varied considerably within the range of compositions investigated. The majority of the data on Zn loss by mass balance calculations is between 30 and 70 pct (table 1). A majority of data in table 2 indicate that less than 2 pct of the Zn is retained in the bullion phase (fig. 4B). Average bullion analysis for Zn was 0.017 wt pct for this fraction. The distribution of Zn

between bullion and slag also appears to be independent of slag composition.

Cadmium was the most volatile of the minor elements studied. Calculated loss of Cd by volatilization is summarized in table 1. An average Cd loss was calculated to be 92.8 pct. In table 2, for the small fraction of Cd retained in the system, the majority of the data indicated

that 60 pct or more of the retained Cd reports to the bullion (fig. 4C). This is of minor consequence in view of the degree of volatilization.

The calculated loss of Co varied considerably within the compositions investigated, 20 to 80 pct (table 1), but did not follow any trend. Cobalt would not be volatilized from the system, thus calculated losses reflect in analytical uncertainty due to the small amount of Co in the system. If all the Co reported to the slag phase, slag analyses would be approximately 0.06 wt pct, thus a difference in 0.03 wt pct in the analysis would account for a 50-pct change in Co for mass balance. Mass balance calculations showed that for the majority of the data, less than 6 pct of the retained Co in the system reported to the bullion (fig. 4D). These data are summarized in table 2, and the retention of Co in the bullion appeared to be independent of slag composition.

It is significant that none of the minor elements studied appear to show any sensitivity to retention owing to slag composition over the range studied. The slag composition distinctly affects the melting and viscosity of the slag, and the metal retention is clearly related to the capability of

the bullion globules to settle. The escape of volatile constituents takes place regardless. As shown in figure 2, at any constant  $\text{SiO}_2 + \text{MgO}$  composition, the viscosity steadily decreases with an increase in CaO concentration. At 25 wt pct CaO and at  $\text{SiO}_2 + \text{MgO}$  concentrations of less than 6 wt pct, the slag is very fluid. A slag composition with a CaO content greater than 28 wt pct and combined  $\text{SiO}_2 + \text{MgO}$  concentration of 6 wt pct or less is not only very fluid, but also very corrosive at  $1,250^\circ\text{C}$ . The presence of Zn in concentrations used here has not been identified as detrimental to the fluidity of the slag, neither is there any apparent correlation between the presence of Zn and the behavior of the other minor elements. Developments in this study indicate that the possible undesirable effects of small amounts of  $\text{SiO}_2$  and Zn on the Pb losses to the slag may be alleviated by dilution with CaO to a total slag CaO concentration of approximately 28 wt pct.

A study of the influence of S, i.e., PbS or PbS concentrate, on the reduction of the sulfide to Pb bullion and the influence of minor elements using the calcium ferrite slag currently is underway.

## CONCLUSIONS

The effects of calcium ferrite slag composition on the retention of Pb in the slag and the distribution of minor elements between the bullion and ferrite slag were studied at  $1,250^\circ\text{C}$ . Experimental results attest to the usability of the calcium ferrite slag in the smelting of PbS concentrates. Conclusions from this investigation are as follows:

1. The retention of Pb in the ferrite slag is low, typically less than 1 wt pct Pb in the slag, which compares with 6 wt pct Pb (6 times less) in iron silicate slags under similar conditions. In the range examined, slag composition did not have an effect (see figure 3) on the retention of Pb in the slag. However, slag composition influenced the melting point and viscosity of the slag, which would clearly relate to the capability of the bullion globules to settle and form a separate bullion phase.

2. Slag composition did not correlate with the distribution of minor elements Co, Cd, Zn, and Ag between the Pb bullion and slag phases. The escape of volatile constituents takes place regardless of slag composition. Approximately 98 pct of the retained Ag, less than 2 pct of the retained Zn, less than 6 pct of the retained Co, and more than 60 pct of the retained Cd reports to the Pb bullion phase.

3. The presence of Zn and  $\text{SiO}_2$  in the concentrations used here has not been identified as detrimental to the fluidity of the slag. There is no correlation between the presence of Zn and the behavior of the other minor elements. Possible undesirable effects of small amounts of Zn and  $\text{SiO}_2$  on Pb losses to the slag because of decreased fluidity could be alleviated by dilution of the slag with CaO to a total slag CaO concentration of an approximately 28 wt pct.

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**APPENDIX.—SUMMARY OF CHEMICAL ANALYSES OF BULLION  
AND SLAG, WEIGHT PERCENT**

Run <sup>1</sup>	Bullion				Slag				
	Co	Cd	Zn	Ag	Co	Cd	Zn	Ag	Pb
16-2-1 ..	0.004	0.140	0.020	3.010	0.040	0.010	0.350	0.010	0.890
16-2-2 ..	.004	.160	.020	2.790	.077	.006	.380	.039	.640
16-4-1 ..	.010	.007	.030	2.560	.060	.003	.530	.004	.480
16-4-2 ..	.005	.030	.020	2.550	.030	.003	.370	.010	.610
16-6 ....	.007	.008	.030	2.780	.060	.005	.320	.004	.620
16-8 ....	.040	.002	.110	2.520	.020	.003	.020	.002	.086
16-10 ...	.070	.003	.260	2.740	.020	.003	.020	.002	.042
18-2 ....	.003	.270	.010	2.840	.074	.011	.380	.005	.800
18-4-1 ..	.006	.003	.030	2.670	.080	.007	.400	.003	.250
18-4-2 ..	.001	.170	.005	3.120	.070	.020	.470	.010	.820
18-6 ....	.010	.003	.100	2.590	.040	.007	.190	.005	.340
18-8 ....	.020	.002	.060	2.380	.040	.006	.100	.002	.130
20-2 ....	.002	.180	.007	2.970	.040	.006	.300	.010	.530
20-4 ....	.002	.240	.003	2.420	.070	.006	.340	.003	.220
20-6-1 ..	.007	.160	.020	2.650	.030	.004	.300	.002	.130
20-6-2 ..	.030	.020	.080	1.960	.027	.001	.260	.001	.085
20-8 ....	.010	.170	.040	2.570	.020	.004	.060	.002	.044
22-4 ....	.005	.040	.020	2.670	.030	.003	.520	.007	.310
22-6-1 ..	.005	.076	.008	2.610	.013	.002	.200	.003	.180
22-6-2 ..	.008	.210	.020	2.590	.040	.004	.220	.002	.180
22-8-1 ..	.010	.250	.020	2.620	.030	.005	.220	.003	.140
22-8-2 ..	.004	.002	.007	2.650	.018	.001	.150	.001	.084
22-10 ...	.038	.001	.270	2.410	.027	.004	.190	.012	.180
24-4 ....	.002	.084	.008	2.700	.038	.002	.270	.002	.150
24-6 ....	.003	.097	.007	2.700	.033	.002	.220	.006	.230
24-8 ....	.009	.032	.022	2.740	.018	.001	.200	.001	.061
24-10-1 .	.020	.020	.070	2.430	.020	.002	.220	.003	.056
24-10-2 .	.024	.130	.100	2.560	.031	.004	.140	.005	.110
26-2-1 ..	.002	.600	.008	2.910	.030	.010	.340	.020	.320
26-2-2 ..	.002	.400	.008	2.360	.050	.009	.370	.010	.520
26-4 ....	.002	.016	.002	2.590	.015	.001	.210	.001	.067
26-6-1 ..	.005	.550	.018	2.180	.061	.016	.340	.006	.480
26-6-2 ..	.003	.110	.009	2.620	.009	.002	.084	.002	.038
26-8 ....	.004	.120	.010	2.610	.012	.002	.170	.002	.075
28-2-1 ..	.001	.140	.005	2.730	.036	.006	.270	.016	.310
28-2-2 ..	.004	.670	.015	2.550	.040	.007	.310	.003	.200
28-4 ....	.003	.045	.011	2.700	.040	.001	.260	.002	.130
28-6-1 ..	.003	.560	.020	2.640	.070	.010	.350	.003	.200
28-6-2 ..	.003	.013	.015	2.590	.037	.005	.300	.004	.120
28-6-3 ..	.008	.460	.030	2.540	.031	.005	.310	.002	.098
28-8 ....	.010	.240	.031	2.440	.024	.005	.260	.002	.064
30-2-1 ..	.009	.640	.040	2.850	.030	.008	.300	.011	.410
30-2-2 ..	.003	.520	.011	2.600	.030	.008	.300	.011	.410
30-4 ....	.003	.090	.019	2.670	.040	.003	.330	.002	.130
30-6-1 ..	.003	.310	.020	2.420	.056	.010	.380	.001	.130
30-6-2 ..	.005	.120	.010	2.440	.035	.006	.180	.007	.063
30-8-1 ..	.006	.380	.040	2.520	.060	.008	.320	.003	.140
30-8-2 ..	.030	.310	.060	2.260	.024	.005	.270	.001	.055
32-2 ....	.004	.520	.016	2.680	.030	.005	.290	.004	.160
32-4 ....	.003	.041	.011	2.670	.056	.002	.460	.002	.160
32-6-1 ..	.003	.020	.019	2.580	.016	.002	.170	.003	.045
32-6-2 ..	.006	.430	.027	1.890	.022	.010	.280	.005	.049
32-8-1 ..	.008	.080	.017	2.060	.019	.011	.064	.001	.080
32-8-2 ..	.003	.062	.008	2.530	.013	.002	.150	.001	.040

<sup>1</sup>First and second numbers indicate weight percent, respectively, of CaO and SiO<sub>2</sub> + MgO in slag. Third number, if any, indicates multiple tests.