THE DISTILLATION PROCESS OF ZINC, LEAD AND CADMIUM FROM BLACK ORES WITH IRON REDUCTION

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We examined the distillation process of zinc, lead and cadmium from black ores (the complex sulphide ores) with iron reduction. Zinc, lead and cadmium respectively were presented as a sulphide, —ZnS, PbS or CdS— in the black ores. We obtained Zn, Pb and Cd by reducing the ores with iron powder according to the following reaction:

$$MS + Fe = M(gas) + FeS \qquad M;\ Zn,\ Pb \text{ and } Cd$$

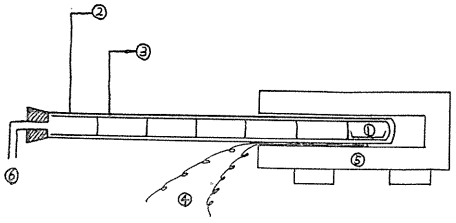
Each metal was separated making use of their condensation points but the separation of Cd from Zn was very difficult. Still, the metal yield percentages were Zn; 97.5%, Pb; 93.3% and Cd; 90.0% at 1200°C, and at 10^{-3} mmHg, and their purities were Zn; 99.1%, and Pb; 98.1% at the same conditions. Optimum conditions were; the reaction temperature 1,200°C, weight ratio of mixture 1 : 1 and the ultimate vacuum 10^{-2}–10^{-3} mmHg.

I. Introduction

Many chemists have tried in the extraction metallurgy[1] of valuable metals in black ores, which are difficult to treat. We already investigated the iron reduction[2] of sulphides of Zn, Pb and Cd. In order to apply the iron reduction process to the black ores, X-ray refraction test of the black ores was carried out. We found that Zn, Cd and Pb were presented as a sulphide of each in the black ores. We understood that the iron reduction process could be applied to the black ores, then we found out that each metal —Zn, Pb or Cd— was produced by each individual condensation of metal vapours after reduction.

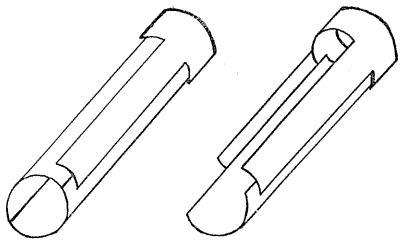
II. Experimental Details

Experimental apparatus: The apparatus is shown in Fig. 1. We charge the sample into the horizontal retort made of stainless steel, and the metal produced



① Sample
② Stainless reaction tube
③ Mild steel or mullite sleeve
④ Thermo-couple
⑤ Siliconit electric furnace
⑥ To vacuum system

FIG. 1. Experimental apparatus.



there is condensed in sleeve separately. We maintain the atmosphere in the retort in vacuum state during the test, and controll the temperature in that place with putting heat insulator. This is shown in details in Fig. 1 and 2.

FIG. 2. Sketch of mild steel sleeve.

Experimental procedure: The composition of the black ore as a sample is Zn; 16.91%, Pb; 3.52%, Cd; 0.57%, SiO_2, As, Fe, Cu, Sb, Bi and so on. The reaction formula is as follows;

$$ZnS+Fe=Zn+FeS,\ PbS+Fe=Pb+FeS,\ CdS+Fe=Cd+FeS$$

We take a porcelain crucible with the mixture of the black ore and iron powder, which is put into a horizontal retort. The retort is pumped to 10^{-3} mmHg. The retort is heated at elevated temperature, maintaining the vacuum state. After a specified time and after cooling in vacuum state, the produced Zn, Pb or Cd metal is taken out and tested in some way. We change the gradient of temperature at the condensation parts. The grain size of ore sample is 100–200 mesh.

As the used range of temperature we selected 1,000°C–1,200°C, at which the reaction for ZnS, PbS, and CdS occurs successfully, and as a reaction time, 5 hr., and we examined the influences of temperature and mixing weight ratio upon the yield percentage of the metals.

III. Experimental Results

Influences of the reaction temperature upon the yield percentage of the metals (Zn, Pb and Cd); The results are shown in Fig. 3. At lower temperature during 1,000°C–1,200°C, the yield percentages of cadmium are good, and at higher temperature the yield percentages of zinc increase better than the other metals. In lead low temperature is not suitable. The yield percentages of the metals at 1,200°C are Zn; 97.5%, Pb; 93.3%, and Cd; 90.0%. The higher the temperature, the higher the yield percentage is. The reaction velocity increases in higher temperature because the reaction occurs easily at higher temperature. From this we selected 1,200°C as a reaction temperature for the following experiments.

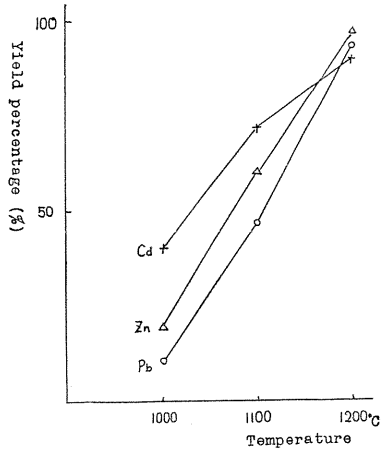


FIG. 3. Relation between yield percentage and reaction temperature.

Influences of the mixing weight ratio (black ore: iron powder); The results

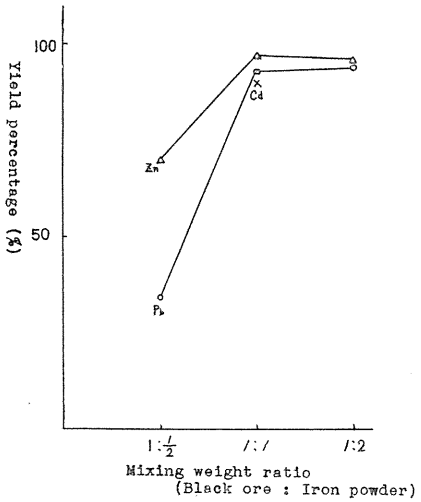


FIG. 4. Relation between yield percentage and mixing weight ratio.

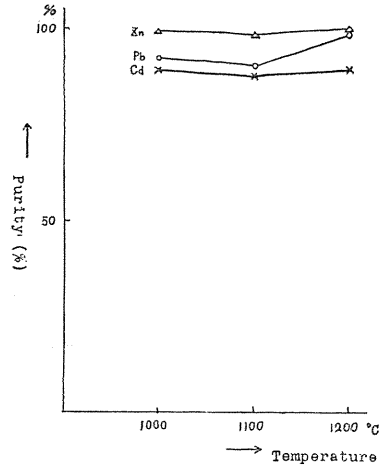


FIG. 5. Relation between reaction temperature and purity.

are shown in Fig. 4. The yield percentages are high at 1 : 1/2–1 : 2 (and the highest yield percentage was given at 1 : 1 and decrease pretty at 1 : 1/2, when the yield percentages are Zn; 70.0%, Pb; 34.1%, and decrease much more at 1 : 2 than at 1 : 1 (In the case of Cd, we could test only one sample as its content in black ore is low).

The conditions of the residues in these cases are shown in Fig. 6. At 1 : 2 the residues seemed to be sintered, and therefore the vaporization of Zn, Pb or Cd is disturbed by sintering and also the results at 1 : 1/2 owe to the decrease of available iron. Vapors of Zn, Pb, or Cd come out easily from residues in non-sintering state or molten state of residue, but not in sintering, we think.

Influcnce of the reaction temperature upon the purities of the produced metals; The results are shown in Fig. 5. In this case we select 25 cm/300°C as the gradient of temperature in the condensation parts. Zinc has 99% on an average and Pb has 98.1%, being the purest at 1,200°C. As cadmium is impossible to decide the purity only at 1 run, we did re-distillation of cadmium, which was collected from the several runs of this research. But we could not obtain cadmium at the purity of 90%. But when we reduced the mixture of Zn, Pb and Cd sulphide (1 : 1 : 1 weight ratio) by iron powder, we could obtain a metal, which has respectively Zn; 99.5%, Pb; 98.6% and Cd; 95.1%. It is very difficult to examine cadmium in details in this research.

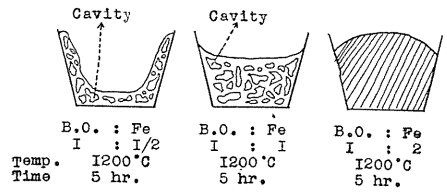


FIG. 6. Sketch of reaction residuse.

Situation of separation by the gradient of temperature at the condensation parts; We did this experiment qualitatively and changed the temperature gradient 11–30 cm/300°C. The results in this case are shown in Fig. 7. At 11 cm/300°C, Pb is thoroughly separated

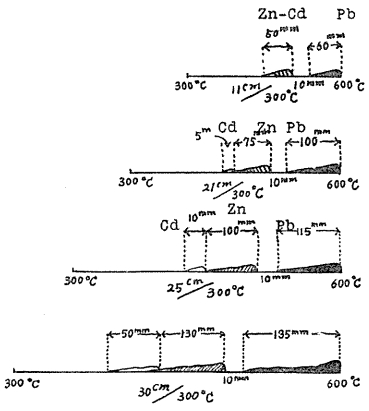


FIG. 7. Situation of separation to the gradient of temperature.

from Zn and Cd, but Zn not from Cd. Although the more lenient the temperature gradient changes so as to be 21, 25 and 30 cm/300°C, the better the situation of separation seems to be. We found that zinc could not be perfectly separated from cadmium by any means.

As stated above, we found that Zn, Pb and Cd in black ores, which are not suitable for smelting, are extracted easily by iron reduction process. In future, we shall publish in more details on this process by which the valuable metals (Zn, Pb and Cd) are availably extracted.

IV. Summary

1) It proceeds availably to extract zinc, lead, and cadmium from the black ores by the distillation process with iron reduction. The optimum conditions are as follows; Reaction temperature 1,200°C, mixing weight ratio 1:1 (black ore: Fe powder), the ultimate vacuum 10^{-2}–10^{-3} mmHg and reaction time 5 hrs.

2) The yield percentages and puries of the metals in this case are as follows;

	Yield percentage (%)	Purity (%)
Zinc	97.5	99.1
Lead	93.3	98.1
Cadmium	90.0	—

3) Vapors of the metals come out easily from residues in non-sintering and molten state. but not in sintering state.

4) The more lenient the temperature gradient during 600°–300°C at condensation parts, the better the situation of separation seems to be.

5) Lead is thoroughly separated from Zn and Cd, but it is difficult for Zn to separate from Cd.

References

1) Y. Ogawa: J. of Min. Metal. Inst. of Japan Vol. 56, 462–465 (1940).
2) H. Sawamoto, T. Sugiura and A. Nishina: Suiyokaishi Vol. 13, No. 7, 558–562 (1958).