Aqueous Oxidation of Zinc Sulfide in Hydrochloric Acid*

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The aqueous oxidation of zinc sulfide in diluted hydrochloric acid was carried out in order to obtain fundamental data on acidic leaching conditions.

Deaerated hydrochloric acid of pH 1~3 and of 10^{-1} ~ 1 mol/L Cl^- was used as acidic media. The amount of zinc sulfide powder suspended in the acidic solution was 10^{-2} ~ 10^{-1} mol/L. The solution was set under certain temperatures between 25° ~ 60°C and stirred at 600 rpm.

Results obtained from the experiment were as follows :

(1) The main dissolution reaction of zinc sulfide in acidic media was of the type of hydrogen sulfide formation and showed a parabolic behavior. The reaction was of diffusion control.

(2) The influence of pH to the dissolution rate of zinc sulfide was linear and the rate of dissolution was decreased with increasing value of pH.

(3) The presence of chloride ion positively influenced the dissolution of zinc sulfide, especially at high temperature.

(4) The relation between the dissolution rate of zinc sulfide and the unit surface area of the ore powder suspended was almost linear. The rate was proportionally increased with increasing area of ore powder.

(5) The dissolution rate of zinc sulfide was large at the initial stage and then decreased with the lapse of time. The rate of dissolution of zinc sulfide was probably decreased with the coexistence of Zn^{2+} in the solution.

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I. Introduction

The development of the direct leaching of sulfide ores is an important investigation in the field of hydrometallurgy. Since the leaching method of sulfide ores in the acidic solution under pressure was presented by Forward⁽¹⁾⁽²⁾, extensive investigations have been carried out by several workers^{(3)~(18)}.

As pointed out recently by Gerlach⁽¹⁹⁾, the theoretical treatment applicable widely to the aqueous oxidation of sulfide ores in acidic media is difficult at present.

But the reaction in aqueous solution can readily be understood thermodynamically by using the potential-pH diagram proposed by Pourbaix⁽²⁰⁾. The diagram was useful in explaining the mechanism of sulfiding corrosion⁽²¹⁾ and of the reaction in extraction metallurgy⁽²²⁾⁽²³⁾.

Though several works have been reported, many fundamental studies are needed to clarify the mechanism of hydrometallurgical reactions in acidic leaching conditions.

The author studied kinetics of the dissolution behavior

of zinc sulfide in hydrochloric acid in order to systematically explain the aqueous oxidation of sulfide ores in acidic media.

II. Experimental

1. Materials

The specimen was prepared from zinc sulfide of chemical grade and was screened to the size of 150 mesh. The chemical composition of the specimen was of nearly theoretical values (Zn: 66.5 wt%, S: 33.45 wt%).

The specimen was analyzed by X-ray diffraction and its X-ray pattern showed both Sphalerite and Wurtzite. The specific surface area of zinc sulfide powder measured by the BET method was varied between 3.3×10^3 and $3.8 \times 10^3 \text{ cm}^2/\text{g}$, and $3.5 \times 10^3 \text{ cm}^2/\text{g}$ was adopted as its standard value. After drying at 40°C , the specimen was used for the experiment. The zinc sulfide powder suspended in the test solution amounted to 10^{-2} ~ 10^{-1} mol/L.

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(1) F. A. Forward and H. Veltman : J. Metals, **11** (1959), 836.

(2) F. A. Forward and I. H. Warren : Metallurgical Reviews, **5** (1959), 137.

(3) Y. Umetsu and K. Tozawa : J. Min. Met. Inst. Japan, **80** (1964), 21.

(4) S. Okamura : *ibid*, **80** (1964), 689.

(5) Y. Hisamatsu and N. Masuko : Electrochemical Soc. Japan, **31** (1963), 771.

(6) F. A. Forward and V. N. Mackiw : Trans. AIME, **203** (1955), 457.

(7) M. Itizô, K. Ôsaki and K. Murayama : J. Min. Met. Inst. Japan, **83** (1967), 594.

(8) N. Masuko and Y. Hisamatsu : *ibid*, **81** (1965), 1153.

(9) K. Azuma, S. Goto, S. Kameda and I. Asakura : *ibid*, **81** (1965), 262.

(10) K. Azuma, S. Goto, S. Kameda and I. Asakura : *ibid*, **83** (1967), 590.

(11) H. Majima and E. Peters : Trans. Met. Soc. AIME, **236** (1966), 1409.

(12) T. R. Scott and N. F. Dyson : *ibid*, **242** (1968), 1815.

(13) A. Vizsolyi, H. Veltman and F. A. Forward : *ibid*, **227** (1963), 215.

(14) D. R. Mackay and J. Helpen : Trans. Met. Soc. AIME, **212** (1958), 301.

(15) K. J. Jackson and J. D. H. Strickland : *ibid*, **212** (1958), 373.

(16) J. Gerlach, H. Hähne and F. Pawlek : Z. Erz. Met., **18** (1965), 73.

(17) J. Gerlach and F. Pawlek : *ibid*, **18** (1965), 509.

(18) J. Dahms, J. Gerlach and F. Pawlek : Z. Erz. Met., **20** (1967), 203.

(19) J. Gerlach : Metall, **16** (1962), 1171.

(20) M. Pourbaix : *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, (1966), p. 545.

(21) J. Horvath and M. Novak : Corr. Sci., **4** (1964), 159.

(22) Y. Hisamatsu and N. Masuko : Metal, **29** (1959), 213.

(23) A. Yazawa : J. Japan Inst. Metals, **31** (1967), 1158.

2. Preparation of the test solution

The test solution with pH 1~3 and Cl^- concentration of 10^{-1} ~1 mol/L was prepared from sodium chloride, hydrochloric acid and distilled water.

3. Experimental procedure

The apparatus used is shown in Fig. 1. The reaction vessel of pyrex glass was of about 2 liter. The vessel was set in a thermostat and the content was stirred at a speed of 600 rpm by the magnetic stirrer. After nitrogen gas was passed in the vessel in order to replace oxygen and a known weight of zinc sulfide ore was quickly added in the solution.

Nitrogen gas was passed at a speed of 200 mL/min throughout whole experiments to remove hydrogen sulfide gas generated. At a certain interval, analytical samples were extracted from the vessel and analyzed by the EDTA titration method⁽²⁴⁾

Fig. 1 Block diagram of the apparatus.

III. Experimental Results

1. Kinetic dissolution behavior of zinc sulfide in acidic media

According to equilibrium theory, the dissolution mechanism of zinc sulfide in acidic media is divided into the three reactions, i.e. H_2S formation type, S^0 formation type and SO_4^{2-} formation type.

The diluted hydrochloric acid is better than sulfuric acid to obtain the data on the accurate dissolution behavior of zinc sulfide in acidic media.

In the preliminary test, extraction behaviors of zinc sulfide in diluted HCl and H_2SO_4 were compared with the result that the reaction types of zinc sulfide dissolution were the same in both acids. So the dissolution was carried out only in diluted HCl. The effective factors on dissolution are considered to be pH, the concentration of chloride ion, temperature, and the amount of zinc sulfide suspended in the solution.

The experiments were carried out to determine these factors.

The effect of pH on the dissolution is shown in Fig. 2.

The dissolution of zinc sulfide in acidic media is large in the initial stage, and decreases with the lapse of time, showing a parabolic curve as a whole. The concentration of Zn^{2+} dissolved in the solution is affected by pH values and the extraction rate is decreased with increasing value of pH.

In Fig. 3 an example of the influence of chloride ion concentration on the dissolution is shown. The extraction of Zn^{2+} are increased with increasing concentration of chloride ion in the solution at 60°C , but extraction rates of Zn^{2+} are small in the range of high pH values, especially at low temperature.

Fig. 2 Effect of pH on the dissolution of zinc sulfide in dilute HCl solution.

Fig. 3 Effect of Cl^- ion on the dissolution of zinc sulfide in dilute HCl solution.

An example of the effect of temperature on the dissolution is shown in Fig. 4. The extraction amount of Zn^{2+} is increased proportionally with elevating temperature, but the influence of temperature is not marked at high pH values.

On the other hand, the dissolution of zinc sulfide was determined in the solution of pH 1 at 60°C to obtain the influence of Zn^{2+} coexisting in the solution and the result is shown in Fig. 5. When Zn^{2+} coexists in the solution, the dissolution of zinc sulfide is inhibited in proportion to the amount of Zn^{2+} added in the solution.

An example of the influence of the amount of suspended zinc sulfide particle on the dissolution rate is shown in Fig. 6. The dissolution rate of zinc sulfide was

Fig. 4 Effect of temperature on the dissolution of zinc sulfide in dilute HCl solution.

Fig. 5 Effect of additional Zn^{2+} ion on the dissolution of zinc sulfide in dilute HCl solution.

Fig. 6 Effect of the amount of suspended zinc sulfide on the dissolution in dilute HCl solution.

increased linearly with increasing specific surface area of ore particle in the solution.

2. Behavior of sulfur

Both sulfate and sulfur formations of zinc sulfide in acidic media were analyzed by measurements of barium sulfate weight and X-ray diffraction. But, SO_4^{2-} in the solution and the S^0 formation in the precipitate could not be seen. A small quantity of amorphous sulfur was only found in the precipitate by extraction with pyridin.

3. Equilibrium potential of the platinum electrode in acidic solution saturated with hydrogen sulfide gas

In the above experiments, the dissolution of zinc sulfide in acidic leaching solution was measured by volumetric analysis and X-ray diffraction and the main reaction was concluded to be of the H_2S formation type in the experimental conditions. The equilibrium potential of the platinum electrode immersed in the acidic solution containing zinc sulfide and saturated with hydrogen sulfide gas was determined according to reference (5).

As shown in Fig. 7 the pH dependence of potentials (dE/dpH) was 120 mV in the region of pH 0~1.5 and 58 mV in pH 1.5~4.

In the low pH solutions the pH dependence of potentials was twice greater than that in the high pH solutions, but both solutions showed a similar redox potential of the S/H_2S system.

On the other hand, the electrode potential of the platinum electrode in acidic solution containing zinc sulfide and saturated hydrogen sulfide gas showed a noble potential value at the initial stage and then shifted rapidly to the basic potential side. But the potential showed similar values in redox potential of the S/H_2S system and was not affected by the amount of zinc sulfide suspended.

Fig. 7 Effect of additional zinc sulfide on the equilibrium potential of the Pt electrode in acidic solution containing 1M Cl^- and saturated with H_2S .

IV. Discussion

In the acidic solution with no oxygen, the dissolution of zinc sulfide was considered to be the reaction type of hydrogen sulfide formation from the experiments (1~3) at high temperature, but according to equilibrium theory, this type of reaction could be discussed by the potential-pH diagram of the $Zn-S-H_2O$ system. This diagram was made out on the basis of the calculation of Latimer's data⁽²⁵⁾, as shown in Fig. 8. This coincided to the experimental results that in such high solubility sulfides

(25) W. M. Latimer : *Oxidation Potentials*, Second Ed., Prentice-Hall, Inc., (1952), p. 168.

Fig. 8 Potential-pH diagram of Zn-S-H₂O system at 25°C.

- ① (H_2S)= 10^{-1} (P_{H_2S} =1 atm) ② (H_2S)= 10^{-1} , (Zn^{2+})=1
 ③ (Zn^{2+})=1 ④ (H_2S)= 10^{-3} ⑤ (H_2S)= 10^{-3} , (Zn^{2+})=1
 ⑥ (H_2S)= 10^{-1} , (Zn^{2+})= 10^{-3} ⑦ (Zn^{2+})= 10^{-1} ⑧ (Zn^{2+})= 10^{-2}
 ⑨ (Zn^{2+})= 10^{-3} ⑩ (HSO_4^-)=1 ⑪ (SO_4^{2-})=1

as zinc sulfide, the reaction type of hydrogen sulfide formation took place predominantly in the deaerated solution of low pH and at high temperature.

The extraction behavior of zinc sulfide under an acidic leaching condition can be expected according to equilibrium theory, providing useful information in the field of hydrometallurgy from the kinetic point of view. Kinetic analysis of the extraction of zinc sulfide was carried out as follows. As shown in Figs. 2~6, the dissolution of zinc sulfide is large in the first step and the concentration of Zn^{2+} dissolved increases with time. The reaction is considered to be a mono-molecular reaction, and the data were treated by linear law.

As shown in Fig. 9, the concentration of zinc sulfide in the solution decreases with time and the dissolution rate of zinc sulfide increases with temperature.

An Arrhenius plot of the rate constant k with temperature is shown in Fig. 10. The apparent activation energy was obtained to be 5.64×10^3 cal/mol and this value corresponds to the diffusion control of ion in the solution.

In Fig. 11, a parabolic plot of the dissolution of zinc sulfide is shown as an example. The kinetics of extraction of zinc sulfide is essentially governed by the diffusion of ion in the solution and is thus of the form,

Fig. 9 Relation between the dissolution of ZnS and time.

Fig. 10 Relation between the dissolution rate constant of ZnS and temperature of dilute HCl solution.

Fig. 11 Parabolic plot of the dissolution of ZnS in dilute HCl solution.

$$Ns = k_1 \times t^{1/2} \quad (1)$$

where Ns is moles of Zn^{2+} dissolved, k_1 a constant, and t the time in minute.

By differentiation of (1),

$$dNs/dt = \frac{1}{2} k_1 \times t^{-1/2}. \quad (2)$$

If the constant $\left(\frac{1}{2} k_1\right)$ is replaced by k_2 , eq. (2) is followingly

$$dNs/dt = k_2 \times t^{-1/2} \quad (3)$$

from (3) the rate constant k_2 can be calculated. If $Ns/t^{1/2} = r_0$,

$$r_0 \propto k_2. \quad (4)$$

Hence, the parameter r_0 can be taken instead of k_2 , and then several effective factors on the kinetics of the dissolution behavior of zinc sulfide in the acidic leaching condition are discussed.

The effect of acidity on the kinetic dissolution behavior of zinc sulfide is shown in Fig. 12, which can be expressed by the equation,

$$\log r_0 = \alpha \log aH^+ + \beta \quad (5)$$

where α and β are constants and a is the activity of hydrogen ion.

The effect of temperature on the constant (α) is rather

Fig. 12 Relation between the r_0 and the pH of dilute HCl solution containing 1 M Cl^- .

Fig. 13 Relation between r_0 and the concentration of Cl^- in dilute solution of $\text{pH}=1$.

small at low temperature but increased with temperature. The value of α is about 1 at 60°C. As shown in Fig. 13, the correlation between r_0 and the concentration of chloride ion in diluted solution is linear and the value of r_0 is increased proportionally with increasing concentration of chloride ion in the solution.

But the dependence of r_0 on chloride ion is varied with temperature, being relatively small at low temperature and large at high temperature.

The effect of chloride on the rate is increased with elevating temperature.

The relations among the specific surface area of ore particles, the extraction rate and the suspended state of ore in the solution are shown in Fig. 14 and the following equation is obtained:

$$\log r_0 = \delta \cdot A/V + \epsilon, \quad (6)$$

where A is the specific area of ore particle, V the volume of leaching solution, and δ and ϵ are constants. The extraction rate of zinc sulfide is increased with increasing specific area of ore in unit concentration of the acid and the reaction is considered a typical heterogeneous process which shows a strong dependence on the surface of zinc sulfide.

On the other hand, the effect of addition of Zn^{2+} on the extraction rate is shown in Fig. 15. The reaction rate is decreased with increasing addition of Zn^{2+} in the

Fig. 14 Relation between $\log r_0$ and the surface area of ore in dilute HCl solution of $\text{pH}=1$.

Fig. 15 Relation between the r_0 and the concentration of Zn^{2+} added in dilute HCl solution of $\text{pH}=1$ at 60°C.

solution, and the dissolution of zinc sulfide is suppressed.

One of the reasons for the decreasing rate with time is considered to be due to the inhibition of dissolution with increasing concentration of Zn^{2+} coexisting in the solution.

The kinetics of the dissolution reaction of zinc sulfide is discussed according to rate theory and the dissolution of zinc sulfide under the condition measured is of a type of hydrogen sulfide evolution as expressed by

From the results determined, factors of the extraction reaction of zinc sulfide are considered as diffusion control of ion in the solution or transport control. The fact that the reaction is affected by stirring velocity should be understood. A similar conclusion on the kinetic study on extraction of pyrite in the acidic leaching condition has been made elsewhere⁽²⁶⁾.

On the other hand, the equilibrium potential of the platinum electrode immersed in the zinc sulfide suspended

(26) M. I. Sherman and J. D. H. Strickland: Trans. AIME, 209 (1957), 1386.

solution shows a value close to the potential of the S/H₂S system in case of the existence of hydrogen sulfide and the main extraction reaction of zinc sulfide is considered to obey eq. (7).

The reason for the anion effect to increase the dissolution rate of zinc sulfide is considered as the activation of the interface of zinc sulfide by chloride ion.

V. Conclusion

Factors which affect the dissolution of zinc sulfide in hydrochloric acid are analyzed from a kinetic point of view and the results obtained are concluded as follows:

(1) The main dissolution reaction of zinc sulfide in the

acidic solution is of a type of hydrogen sulfide formation and shows a parabolic behavior. The reaction is of diffusion control.

(2) The effect of pH on the dissolution rate of zinc sulfide is linear and the rate of dissolution decreases with increasing value of pH.

(3) The presence of chloride ion positively affects the extraction of zinc sulfide, especially at high temperature.

(4) The relation between the extraction rate of zinc sulfide and the surface area of ore particles suspended in the solution is linear and the rate increases proportionally with increasing area of the ore.

(5) The dissolution rate of zinc sulfide is large at the first stage and decreases with time. The rate is decreased under the coexistence of Zn²⁺ in the solution.