

# Study on the pH Dependence for Copper Activation of Sphalerite

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## Abstract

The pH dependence of copper activation on sphalerite was studied by measuring the adsorption of copper ions as a function of pH. The adsorption of copper ions was maximum at about pH 5~6 and decreased rapidly in both the acid and alkaline region. From the results obtained, it was recognized that the pH dependence for the adsorption of copper ions on sphalerite was remarkable.

The cause for the decrease of the copper adsorption on sphalerite in the alkaline region was investigated. The dependence of concentration of copper ions in the solution for the copper adsorption on sphalerite was examined. From the results, it was recognized that the copper adsorption on sphalerite decreased with a lowering of the concentration of copper ions in the solution.

Then, the kinetics for the adsorption of copper ions on sphalerite was investigated. The reaction rate of the copper adsorption on sphalerite was shown by the reaction equation of the 1st order, and the relationship between the adsorption rate of copper ions on sphalerite and the agitation rate was characterized by a straight line in the log-log plot.

The above results suggested that the decrease of the copper adsorption on sphalerite in the alkaline region might be due to the decrease of the copper concentration in the solution with the increase of the pH value, and consequently to the decrease of the diffusion rate at which the copper ions diffused to the surface of sphalerite from the bulk in the solution.

The cause for the decrease of the copper ions in the acid region was analysed experimentally. With regard to the results, it was surmised that the formation of copper sulphide led to the decrease of the copper concentration in the solution. The formation of copper sulphide was caused by the generation of  $H_2S$  resulting in the dissolution of sphalerite in the acid solution. Accordingly, there was a decrease of the copper concentration in the solution and of the diffusion rate of copper ions.

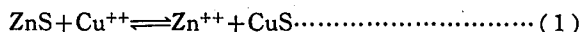
As mentioned above, the reaction rate of the copper adsorption on sphalerite was determined by the diffusion rate of copper ions.

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## 1. Introduction

The copper activation on sphalerite has been studied by many investigators, and the results have been shown to come from the following reaction.



C. H. G. Bushell and C. J. Krauss<sup>1)</sup> had stated that from thermodynamic calculations the copper activation on pyrite could not be prevented by the OH<sup>-</sup> ion. Similar calculations of copper activation reaction on sphalerite were indicated by the author that the equation (1) would proceed all pH ranges.

On the other hand, S. I. Mitrofanov and V. G. Kushnikova<sup>2)</sup> had showed by experiments that the adsorption of copper ions on pyrrhotite was maximum at about pH 6, and decreased rapidly with the increase of pH. As a consequence, they concluded that the adsorption of copper ions on pyrrhotite depended on the pH value. T. W. Holmsen<sup>3)</sup> also had presented a similar explanation about pyrrhotite on the adsorption of copper ions for sphalerite.

As mentioned above, the different views have been explained as to the effect of pH for the copper adsorption of sphalerite. In this paper, the effect of pH for the copper adsorption of sphalerite was studied experimentally.

## 2. Preparation of Mineral Sample

Sphalerite from the Toyoha mine in Hokkaido, Japan, was used in this experiment. Coarse pieces of high grade sphalerite were selected and crushed. Then, pure sphalerite particles were picked up by hand and ground in an agate mortar. The ground sphalerite was sieved and the 65~100 mesh fraction was prepared. Also more contaminants, such as quartz, galena, and pyrite, were removed by the Frantz isodynamic magnetic separator. The purified sample was washed repeatedly in distilled water in order to eliminate fine particles of <10 micron. This sample was used for the experiment after being dried in a vacuum desiccator.

## 3. Experimental Procedure and Results

### 3. 1. Effect of pH on Copper Adsorption of Sphalerite.

One gram of the 65~100 mesh sphalerite weighed accurately was added to 50 ml of a copper sulphate solution of  $1 \times 10^{-4}$  mole/l, which was adjusted to the given pH values. After the mixture was kept in a thermostat at temperature of 25°C for a given time, the excessive copper ions and copper hydroxide were removed by the decantation method. The sphalerite sample was washed thoroughly with distilled water. The copper activated sphalerite was treated with sodium cyanide solution, and the adsorbed products on sphalerite were leached. The copper adsorption on sphalerite was

measured by using the Jarrell-Ash atomic absorption spectrometer. The adjustment of pH values was carried out with Britton and Robinson's buffer solution.<sup>4)</sup> The blank test was carried out by treating the unactivated sphalerite with sodium cyanide solution.

The copper activation on sphalerite was carried out by varying the pH of the solution and the treating time for 1/2~48 hr. The obtained results are shown in Fig. 1. As shown in Fig. 1, the copper adsorption on sphalerite was maximum at pH 5~6 and decreased rapidly with the increase of pH. With the increase of the treating time, the copper adsorption on sphalerite increased over all the pH ranges. In the pH ranges copper hydroxide was formed. However, the copper adsorption on sphalerite decreased remarkably.

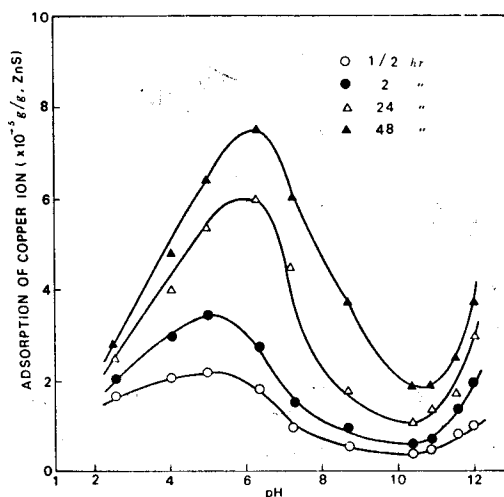


Fig. 1. Effect of the pH on the copper adsorption of sphalerite.

From the above results, the effect of pH on the copper adsorption of sphalerite was remarkable.

### 3. 2. Dependence of Copper Ion Concentration on Copper Adsorption of Sphalerite.

From the above results, it was recognized that the copper adsorption on sphalerite decreased remarkably with an increase of the pH value. On the other hand, copper hydroxide is formed with an increase of the pH value of solution containing copper ions, and then the concentration of free copper ions in the solution is decreased. However, the precipitates of copper hydroxide dissolve again and the copper activation on sphalerite begins to proceed. In this section, the dependence of the concentration of copper ions in the solution on the copper adsorption of sphalerite was examined.

In order to be very similar to the experiment in the late section, the concentra-

tion of copper ions was varied, but the amounts of copper ions contained in each solution were equal. The concentration of copper ions was  $5 \times 10^{-5}$ ,  $1 \times 10^{-5}$  and  $5 \times 10^{-6}$  mole/l, and the volume of solution was 100, 500 and 1,000 ml respectively. The amounts of copper adsorption on sphalerite was measured with the lapse of time under the fixed condition of pH 6.37.

The results obtained are shown in Fig. 2. As shown in Fig. 2, the copper adsorp-

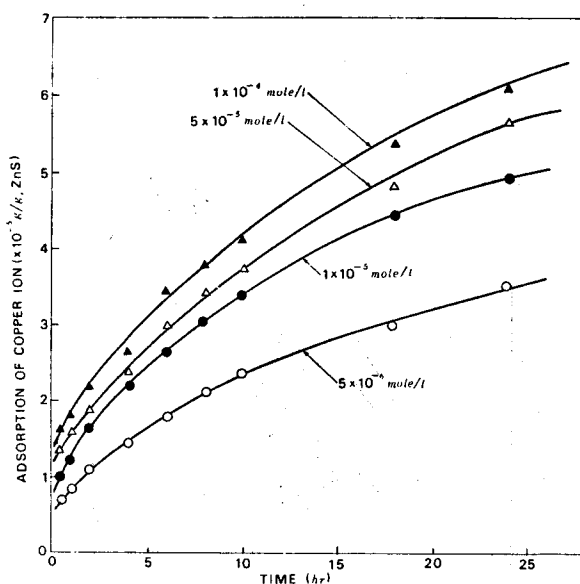


Fig. 2. Relationship between the treating time and copper adsorption on sphalerite.

tion on sphalerite lowered remarkably with the decrease of the initial concentration of copper ions. It means that the copper adsorption on sphalerite depends on the concentration of copper ions in the solution.

In the pH region of formed copper hydroxide, if the pH value is given, the copper ion concentration in equilibrium state can be calculated from the solubility product of copper hydroxide ( $=1.6 \times 10^{-19}$ ).<sup>\*</sup> When the copper ion concentration in equilibrium is  $5 \times 10^{-5}$ ,  $1 \times 10^{-5}$  and  $5 \times 10^{-6}$  mole/l, the pH value resulting from the calculation is 6.75, 7.10 and 7.25 respectively. The copper adsorption on sphalerite for each of the above pH values is determined from Fig. 1. The results obtained are shown in Table 1. As shown in Table 1, the copper adsorption on sphalerite with the varying pH value of solution agrees very well with the copper adsorption corresponding with each concentration in Fig. 2.

\* as given by Latimer

Table 1. Relationship between the addition of copper ions and copper adsorption on sphalerite.

ADDITION OF COPPER ION (mole/l)	ADSORPTION OF COPPER ION ( $\times 10^{-5}$ g/g, ZnS)		
	1/2hr	2hr	24hr
$1 \times 10^{-4}$ (pH 6.75)	1.46	2.20	5.60
$5 \times 10^{-5}$ (pH 6.37)	1.45	1.90	5.62
$1 \times 10^{-4}$ (pH 7.10)	1.06	1.70	4.82
$1 \times 10^{-5}$ (pH 6.37)	1.00	1.68	4.86
$1 \times 10^{-4}$ (pH 7.25)	0.98	1.20	3.64
$5 \times 10^{-5}$ (pH 6.37)	0.80	1.15	3.73

From the above results, it is recognized that the decrease of copper adsorption with the increase of pH is caused by a decrease of the concentration of free copper ions in the solution with an increase of pH.

### 3. 3. Effect of Diffusion for Reaction Rate of Copper Adsorption on Sphalerite.

If the reaction rate of copper adsorption on sphalerite is determined by the diffusion rate of copper ions, it will be shown as the following equation on the basis of the Nernst's diffusion law<sup>4)</sup>:

$$dx/dt = k(a-x) \dots \dots \dots (2)$$

where  $a$  is the initial concentration of copper ions and  $x$  is a loss in quantity of copper ions within the time for  $t$ . Integrating equation (2) under the initial condition,  $x=0$  at  $t=0$ , equation (3) is obtained.

$$kt = \ln a/(a-x) \dots \dots \dots (3)$$

As shown in equation (3), the reaction rate of copper adsorption on sphalerite is shown by the equation of the 1st order if it is determined by the diffusion rate of copper ions.

Accordingly, the kinetics for the adsorption of copper ions on sphalerite was investigated by the adsorption reaction of copper ions within the formation of a monolayer.

One gram of 65~100 mesh sphalerite weighed accurately was added to 50 ml of copper sulphate solution of  $1 \times 10^{-5}$  mole/l adjusted at pH 6.37. The copper adsorption on sphalerite was measured with the lapse of time at 25°C.

The specific surface area of 65~100 mesh sphalerite sample was found to be 312 cm<sup>2</sup>/g, as measured by the B. E. T. method. Considering the effective occupied area of copper ion on sphalerite to be 20.8 Å<sup>2</sup>,<sup>7)</sup> the amounts of copper ions require to form a dense monolayer are  $1.58 \times 10^{-5}$  grams per one gram of sphalerite. The results obtained are shown in Table 2. As shown in Table 2, the coverage per cent

Table 2. Coverage of copper adsorption on sphalerite and residual concentration of copper ions with varying the treating time.

TREATING TIME (hr)	ADSORPTION OF COPPER ION ( $\times 10^{-5}$ g/g ZnS)	RESIDUAL CONCENTRATION OF COPPER ION ( $\times 10^{-6}$ mole/l)	COVERAGE (%)
1	0.36	8.87	22.78
2	0.46	8.55	29.11
4	0.60	8.11	37.97
6	0.76	7.61	48.10
8	0.86	7.29	54.43
10	1.00	6.85	63.29
12	1.12	6.48	70.89
14	1.20	6.22	75.95
16	1.32	5.85	83.54
18	1.38	5.66	87.34
20	1.47	5.37	93.04
22	1.50	5.28	94.94
24	1.60	4.96	101.24

varied from 22.78% to 101.27%.

The experimental results were graphed in Fig. 3. Plotting  $\ln a/(a-x)$  against the treating time for  $t$ , the relationship between them are shown by the straight line. The reaction rate of copper adsorption on sphalerite was shown by the reaction

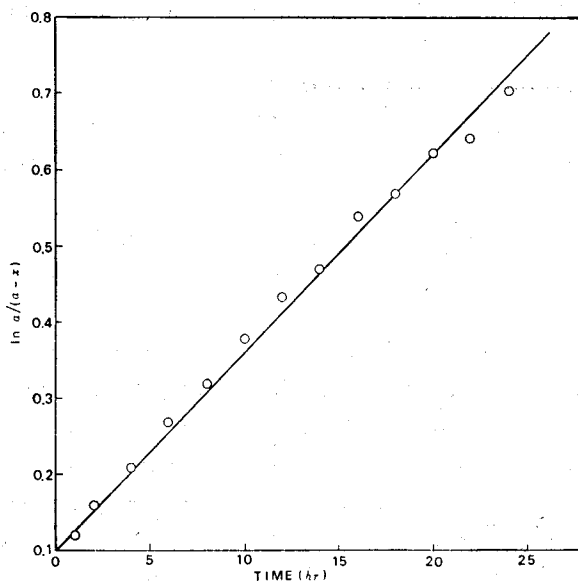


Fig. 3. Relationship between  $\ln a/(a-x)$  and treating time for the copper adsorption.

equation of the 1st order. Accordingly, it was established that our way of thinking, namely, that the diffusion rate determined the adsorption rate of copper ions on sphalerite, was adequate.

The second peculiarity whereby the diffusion rate determines the adsorption rate of copper ions on sphalerite is characterized by the agitation rate governing the adsorption rate.

$$\text{(Adsorption rate)} = (\text{Constant}) \times (\text{Agitation rate})^s \dots \dots \dots (4)$$

Hereupon, the effect of agitation rate for the adsorption rate of copper ions on sphalerite was examined. Using 50 ml of copper ion solution of  $1 \times 10^{-5}$  mole/l and one gram of 65~100 mesh sphalerite, the flow of nitrogen gas was varied and the agitation was carried out for 2 hours. The results obtained are shown in Fig. 4. As shown in Fig. 4, the log-log plot of relationship between the adsorption rate of

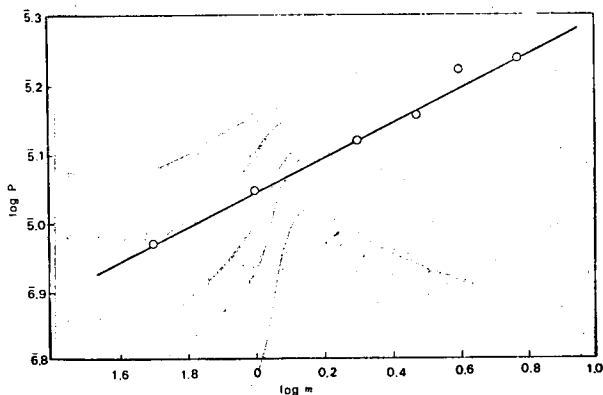


Fig. 4. Relationship between the adsorption rate of copper ions on sphalerite and agitation rate.  
 P : adsorption rate (g/g, ZnS/2hr)  
 m : agitation rate (1/min.)

copper ions on sphalerite and the agitation rate is characterized by a straight line. The value of  $s$  in equation (4), required from Fig. 4, is equal to 0.77.

From the above results, it is clarified that the reaction rate of copper adsorption on sphalerite is presented by the reaction equation of the 1st order, and the adsorption rate of copper ions is determined by the agitation rate. Therefore, the decrease of copper adsorption on sphalerite with an increase of the pH may be due to the decrease of the concentration of free copper ions with an increase of pH. This will lead to the decrease of the diffusion rate of copper ions in the solution.

### 3. 4. Effect of Agitation on Copper Adsorption of Sphalerite.

From the results obtained up to the last section, when the agitation was not practiced in the pH region, copper hydroxide was formed. It was recognized that the

copper adsorption on sphalerite decreased significantly and was governed by the diffusion of copper ions in the solution. From this fact, it is surmised that the reaction of copper activation on sphalerite proceeds well enough, even if the pH value of the solution is sufficiently high and copper hydroxide is present in the pulp. This is because the precipitates of copper hydroxide, of which the solubility is relatively large, are the source of the supply of copper ions.

In this section, the effect of agitation on the copper adsorption of sphalerite was examined in cases of varying the pH values. Using one gram of 65~100 mesh sphalerite and 500 ml of copper sulphate solution of  $1 \times 10^{-5}$  mole/l, the mixture was agitated for 2 hours. A series of tests was carried out by varying the agitation rate differently. The agitation was practiced by using the impeller of a polyethylene make.

The results obtained are shown in Fig. 5. As shown in Fig. 5, it is recognized

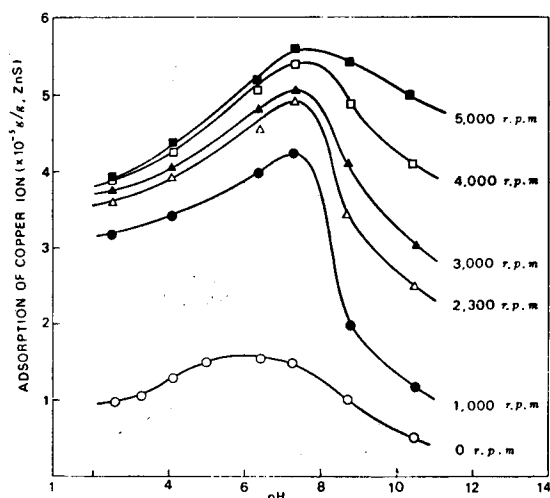


Fig. 5. Effect of the agitation on the copper adsorption of sphalerite.

that the copper adsorption on sphalerite increases with an increase of the agitation rate all pH values, as compared with no agitation. The log-log plot of the relationship between the adsorption rate of copper ions on sphalerite and the agitation rate is shown in Fig. 6. As shown in Fig. 6, it is characterized by a straight line. Consequently it is recognized that equation (4) is established in both the acid and alkaline region. The values of  $s$  in equation (4), required from Fig. 6, are shown in Table 3. As shown in Table 3, the value of  $s$  in the acid region shows the constant value to be about 0.17. It means that the effect of agitation is not so remarkable. In over pH 8.00, the adsorption of copper ions on sphalerite increases with an in-



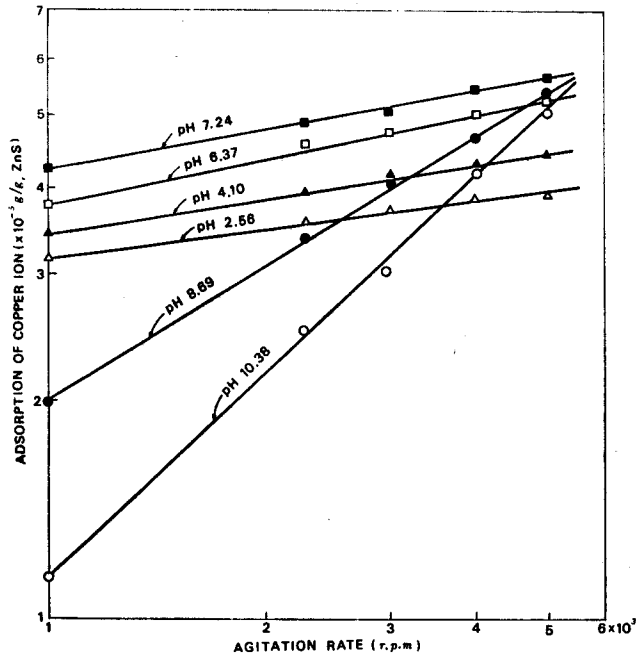


Fig. 6. Relationship between the adsorption rate of copper ions on sphalerite and agitation rate.

Table 3. The values in the equation of adsorption rate.

pH	2.56	4.10	6.37	7.24	8.69	10.38
s	0.129	0.179	0.166	0.175	0.608	0.903

crease of the agitation rate, and also the values of *s* increase remarkably. In particular, the effect of agitation in the alkaline region is remarkable.

3. 5. Cause for Decrease of Copper Adsorption on Sphalerite in Acid Region.

The cause for the decrease of the copper adsorption on sphalerite in the acid region was analysed experimentally. The copper activation reaction is shown generally by reaction (1), and the equilibrium constant of reaction (1) is as follows:

$$K = \frac{[Zn^{++}]}{[Cu^{++}]} = 9 \times 10^{10} \dots \dots \dots (5)$$

The square brackets stand for molar concentrations which are nearly the same as activity at the low concentrations used in flotation.

Accordingly, the copper activation reaction on sphalerite, shown by reaction (1),

\* The equilibrium constant in equation (5) is that given by Gaudin, Fuerstenau and Mao<sup>6)</sup>, and it was calculated from the data given by Latimer. All equilibrium constants used in this paper are based on the data from Latimer unless otherwise noted.

proceeds well only in the case where  $[Zn^{++}]/[Cu^{++}]$  is smaller than the K value of equation (5). It does not proceed well in the contrary case, that is,  $[Zn^{++}]/[Cu^{++}]$  is greater than the K value of equation (5). However, even if the value of  $[Zn^{++}]/[Cu^{++}]$  is smaller than the K value of the equation (5), the thermodynamic driving force for equation (1) becomes small. In consequence, the rate of the copper activation reaction may become slow.

The author considered that the cause for the decrease of the copper adsorption on sphalerite in the acid region led to the decrease of the reaction rate of copper activation due to the generation of zinc ions, resulting in the dissolution of sphalerite in the acid solution. The following experiment was carried out under the above consideration.

Copper sulphate and zinc sulphate were added simultaneously to the suspension of pH 4.10 containing one gram of 65~100 mesh sphalerite and then the total volume of solution was diluted up to 500 ml. The treating temperature was constant at 25°C, and the treating time was for 16 hours. The concentration of copper sulphate was  $1 \times 10^{-5}$  mole/l. The concentration of zinc sulphate was varied differently. The results obtained are shown in Fig. 7. As shown in Fig. 7, in the case where

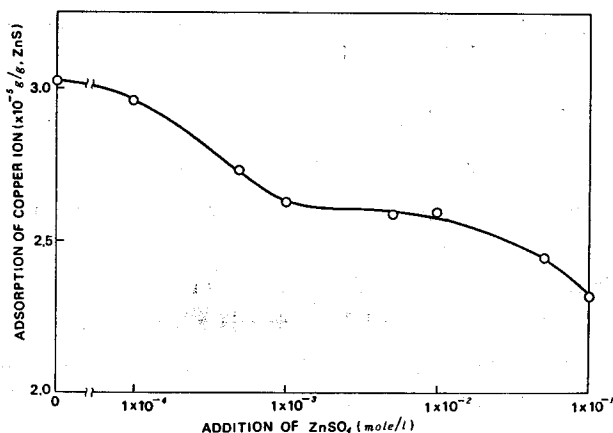


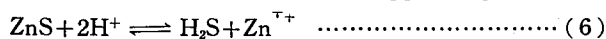
Fig. 7. Effect of zinc sulphate on the copper adsorption of sphalerite.

the concentration of zinc sulphate increases, the copper adsorption on sphalerite does not decrease very much. The adsorption rate of copper ions on sphalerite was extremely slow.

Therefore, the cause for the decrease of the copper adsorption on sphalerite was examined according to the following consideration.

In the acid region of the pH value, sphalerite reacts on the  $H^+$  ion and then  $H_2S$  generates.  $H_2S$  dissociates through the two stages. In consequence, the generated

S<sup>-</sup> ion reacts on the Cu<sup>++</sup> ion and then the copper sulphide generates.



It seems that the concentration of free copper ions in the solution decreases with a lowering of the pH value by the generation of copper sulphate. However, when sphalerite dissolves in the acid solution, a part of the generated H<sub>2</sub>S gas escapes from the reaction system. Accordingly, the concentration of copper ions in the solution containing sphalerite and copper ions was measured at the low pH region.

After one gram of 65~100 mesh sphalerite weighed accurately was added to 500 ml of copper sulphate solution of 1×10<sup>-5</sup> mole/l, the mixture was adjusted at a given pH value. The treatment of copper activation was carried out at 25°C for 24 hours. Then, for the purpose of measuring the residual concentration of copper ions in the solution, the mixture was centrifugally separated at 12,000 rpm by using the ultra-centrifugal separator in order to eliminate the fine precipitates from the mixture. Thus, after the precipitates were eliminated, the concentration of copper ions in the supernatant liquid was measured. The copper adsorption on sphalerite was simultaneously measured by the leaching method using sodium cyanide.

In this case, the material balance is as follows: provided the amounts of copper ions in 500 ml of the original solution are A grams, the amounts of copper adsorption on sphalerite are B grams, the amounts of residual copper ions are C grams, and the amounts of the generated copper sulphide are D grams.

$$A = B + C + D \dots\dots\dots (10)$$

Requiring the amounts of copper sulphide generated on the basis of equation (10), Fig. 8 was obtained. As shown in Fig. 8, it is recognized that the amounts of generated copper sulphide increase considerably with the decrease of pH, and are not relative to the copper adsorption on sphalerite.

The relationship between the residual concentration of copper ions and the copper adsorption in each pH values was required from Fig. 8. The results obtained are shown in Curve I of Fig. 9. As shown in Curve I of Fig. 9, the copper adsorption on sphalerite decreases with the decrease of the residual concentration of copper ions and also with the decrease of the pH value.

The relationship between the residual concentration of copper ions and the copper adsorption was examined experimentally. The experimental procedure was as follows: the original concentration corresponding with 7.21×10<sup>-6</sup>, 7.81×10<sup>-6</sup> and 8.53×10<sup>-6</sup> mole/l of the residual copper ion concentration was previously decided. The volume of solution is three litres, treating time for 24 hours, and treating temperature

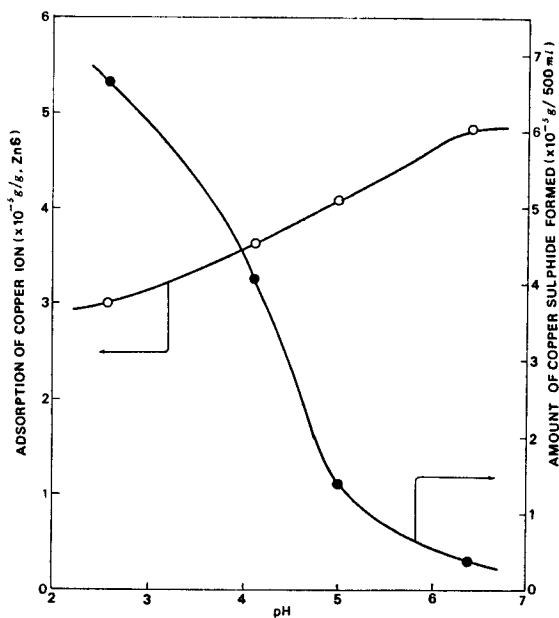


Fig 8. Relationship between the residual concentration of copper ions and copper adsorption on sphalerite as a function of pH.

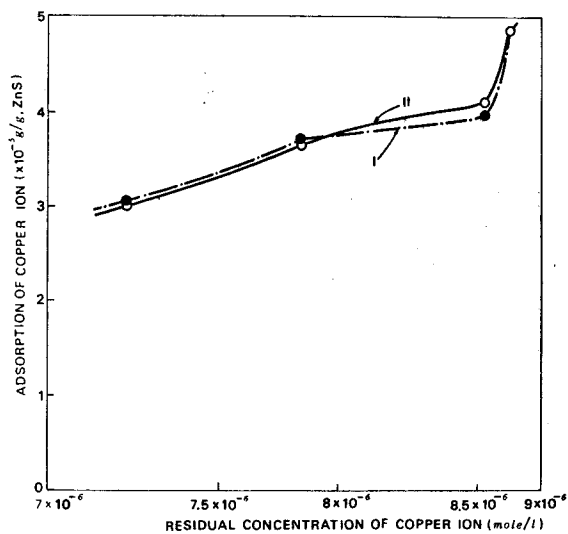


Fig. 9. Relationship between the residual concentration of copper ions and copper adsorption on sphalerite.

I: copper adsorption on sphalerite with varying the pH at  $1 \times 10^{-5}$  mole/l of initial copper concentration.

II: copper adsorption on sphalerite with varying the initial copper concentration at pH 6.37.

at 25°C.

The results obtained are shown in Curve II of Fig. 9. As shown in these results, the difference between Curve I and Curve II was not nearly recognized. As shown in Curve II of Fig. 9, it is recognized that the copper adsorption on sphalerite decreases with the decrease of copper concentration and the dependence on the copper ion concentration is remarkably great. Curve I in Fig. 9 coincides with Curve II in Fig. 9. Therefore, it is surmised that the decrease of copper ions in the acid region is caused by the decrease of the concentration of free copper ions in the solution due to the formation of CuS with the decrease of the pH value, and also due to the decrease of the diffusion rate of copper ions.

#### 4. Conclusions

The effect of pH on the copper adsorption of sphalerite was studied experimentally. The results of this study are summarized as follows:

(1) The adsorption of copper ions on sphalerite was maximum at about pH 5~6, and decreased rapidly in both the acid and alkaline regions. It was recognized that the pH dependence for the adsorption of copper ions on sphalerite was remarkable.

(2) The dependence on the concentration of copper ions for the copper adsorption of sphalerite was examined. It was recognized that the copper adsorption on sphalerite decreased with a lowering of the concentration of copper ions in the solution. From the results obtained, the decrease of the copper adsorption on sphalerite with the increase of the pH was caused by the decrease of the concentration of free copper ions with the increase of the pH.

(3) The kinetics for the adsorption of copper ions on sphalerite were investigated. The reaction rate of the copper adsorption on sphalerite was shown by the reaction equation of the 1st order, and the log-log plot of relationship between the adsorption rate of copper ions on sphalerite and the agitation rate was characterized by a straight line. These results suggested that the decrease of the copper adsorption in the alkaline region might be due to the decrease of the concentration of copper ions with the increase of the pH value. Consequently it would also be due to the decrease of the diffusion rate at which copper ions diffused to the surface of sphalerite from the bulk in solution. The log-log plot of relationship between the copper adsorption rate and the agitation rate was also characterized by a straight line in the acid region.

(4) The cause for the decrease of the copper adsorption on sphalerite in the acid region was analysed experimentally. In consequence, it was surmised that the formation of copper sulphide led to a decrease of the concentration of copper ions in

the solution. The formation of copper sulphide was caused by the generation of  $H_2S$  resulting in the dissolution of sphalerite in the acid solution. Accordingly, the decrease of the copper adsorption on sphalerite in the acid region might be due to the decrease of the concentration of copper ions, and due to the diffusion rate of copper ions.

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