Copper Ion Adsorption on Sphalerites
of Various Iron Contents

By

Yoshitaka NAKAHIRO*

(Received September 21, 1979)

abstract

The kinetics for copper ion adsorption on sphalerites of various iron contents were studied by measuring the adsorption of copper ions in the presence of oxygen and in oxygen free circumstances.

The relationship between the copper ion adsorption rate and the agitation rate was characterized by a straight line in the log-log plot. With the increase of iron contents in the sphalerite, the copper ion adsorption rate on the sphalerite decreased in the case where oxygen was sufficiently dissolved in the copper ion solution and the pH was high enough.

The reaction rate of the copper ion adsorption on sphalerites changed from the rate of a parabolic function to the rate of an exponential function with the increase of iron contents in the sphalerite. As a result, in the above stated conditions, it was surmised that the kinetics for the copper ion adsorption on sphalerites of various iron contents were considerably complex. The kinetics for copper ion adsorption on pyrrhotite were explained by the protective film theory.

From the above results, it may be considered that the dissolved oxygen in the pulp is one of the important factors for the copper activation on sphalerites.

1. Introduction

The pH dependence for the copper activation of a sphalerite with low iron content has been reported in a previous paper[1]. From the experimental results, it was found that the copper activation on sphalerites proceeded in the wide pH ranges with an increase of the agitation rate. However, there are many kinds of sphalerites having various iron contents. Up to now, the characteristics for the copper activation on sphalerites of various iron contents have not been sufficiently known.

In this study, the kinetics for the copper ion adsorption on sphalerites of various iron contents were examined by measuring the adsorption of copper ions in the presence of oxygen and in oxygen-free circumstances.

---

* Department of Mineral Science and Technology

2. Preparation of Mineral Samples

Sphalerite samples from the Toyoha mine in the Hokkaido district, the Taishu mine in Nagasaki prefecture, the Nakadatsu mine in Fukui prefecture, and the Chichibu mine in Saitama prefecture were used in this experiment. Pyrrhotite from the Kawayama mine in Yamaguchi prefecture was also used as a mineral sample for the comparison of sphalerites of various iron contents. Coarse pieces of various sphalerites and pyrrhotite were selected and crushed. Then, pure mineral particles of each of the above samples were picked up by hand and ground in an agate mortar. The ground mineral was sieved and a 65~100 mesh fraction was prepared. The 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. These samples were used for the experiment after being kept in a vacuum desiccator.

The lattice constants of each of the sphalerite samples were measured by the X-ray diffraction method. Sodium chloride was used as an internal standard reagent in order to correct the reflection angle, 2θ. As shown in Table 1, it was found that the lattice constant tended to increase with an increase of iron content in the sphalerite. This is because the increase of iron content in the sphalerite intensifies the tendency of the ionic bond[2]. The values of the lattice constants measured by the present author coincided with the values obtained by H. Mino[3].

Table 1. Iron contents and lattice constants of mineral samples.

MINERAL SAMPLE	Fe(%)	(hkl)	K_α	2 (°′)	d(Å)	a_o(Å)
SPHALERITE (TOYOHA MINE)	0.94	(440)	a_1	138.26	0.95725	5.4150
		(511)	a_1	118.24	1.0422	5.4153
SPHALERITE (TOYOHA MINE)	4.02	(440)	a_1	138.24	0.95731	5.4153
		(511)	a_1	118.18	1.0425	5.4168
SPHALERITE (TAISHU MINE)	7.75	(440)	a_1	138.18	0.95751	5.4164
		(511)	a_1	118.02	1.0434	5.4215
SPHALERITE (NAKADATSU MINE)	10.90	(440)	a_1	137.58	0.95944	5.4274
		(511)	a_1	117.74	1.0449	5.4293
SPHALERITE (CHICHIBU MINE)	16.37	(440)	a_1	137.50	0.95970	5.4288
		(511)	a_1	117.68	1.0452	5.4309
PYRRHOTITE (KAWAYAMAMINE)	57.14	—	—	—	—	—

3. Experimental Procedure and Results

3. 1. Effect of pH on Copper Adsorption on Sphalerites of Various Iron Contents.

One gram of the 65~100 mesh sphalerite weighed accurately was added to 500 ml of a copper sulphate solution of 1×10^{-5} mole/l, which had been preliminarily saturated with nitrogen gas and adjusted to the given pH values. After the mixture was kept in a thermostat at a temperature of 25°C for two hours, the excessive copper ions and copper hydroxide were removed by the decantation method. The sphalerite sample was washed throughly with distilled water. The copper activated sphalerite was treated with a sodium cyanide solution, and the adsorbed products on the sphalerite were leached. The copper adsorption on the 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[4]. The blank test was done by treating the unactivated sphalerite with a sodium cyanide solution.

The results obtained are shown in Fig. 1. As can be seen in Fig. 1, the copper adsorption on the sphalerites was maximum at pH 6~7, regardless of iron contents in the sphalerite, and it decreased with the increase or lowering of pH. Especially, the
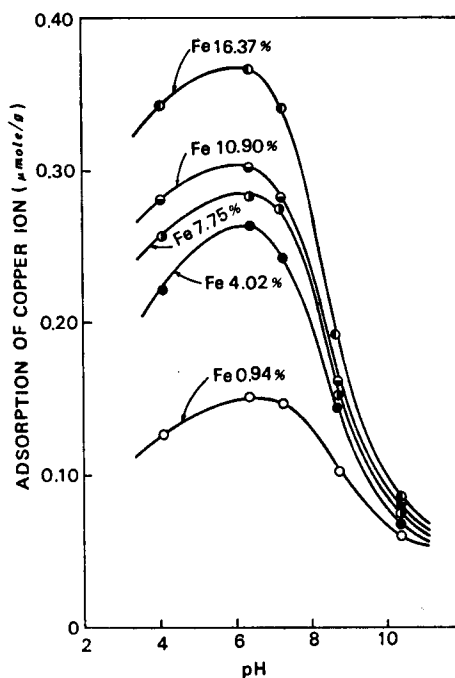

Fig. 1. Effect of the pH on the copper adsorption
of sphalerites of various iron contents.

copper adsorption on the sphalerite decreased remarkably in the pH ranges forming copper hydroxide. From this experiment, it was found that the copper adsorption increased with an increase of iron contents in the sphalerite.

From the above results, the effect of pH on the copper adsorption on sphalerites of various iron contents was remarkable without agitation. As stated in the previous paper[5], this is because the copper adsorption rate of sphalerites without agitation is governed by the diffusion of copper ions in the solution.

3. 2.　Effect of Agitation on Copper Adsorption of Sphalerites of Various Iron Contents.

From the results obtained in the previous section, it is surmised that the reaction of copper activation on sphalerites proceeds sufficiently, even if the pH values of the solution are remarkably high and copper hydroxide forms in the pulp.

In this section, the effect of agitation on the copper adsorption of sphalerites of
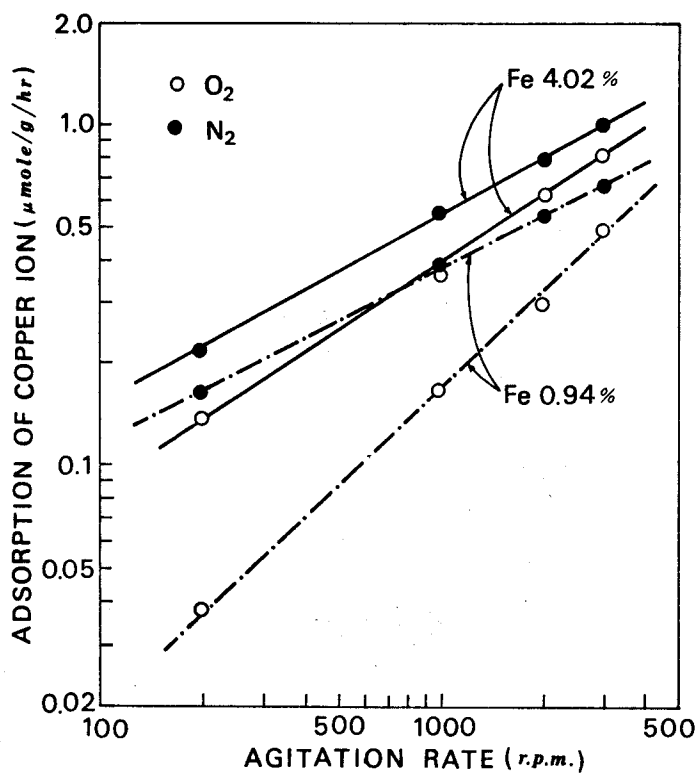

Fig. 2.　Effect of the agitation on the copper adsorption of
sphalerites of Fe 0. 94 % and 4. 02%.

various iron contents was examined under the fixed condition of pH 10. 38. One gram of the 65~100 mesh sphalerite weighed accurately was added to 500 ml of a copper sulphate solution of 1×10^{-5} mole/l, which had been previously saturated with oxygen or nitrogen gas and was adjusted to pH 10. 38. The mixture was agitated for one hour, blowing oxygen or nitrogen gas into the mixture at the flow rate of 100 ml/min. A series of tests was carried out by varying the agitation rate. The agitation was practiced by using the impeller of a polyethylene make.

The results obtained are given in Figs. 2~4. As shown in Figs. 2 and 3, when the iron contents in sphalerites are below 8%, the copper adsorption on the sphalerite increases with the increase of the agitation rate, even if the dissolved oxygen exists in a solution. As shown in Figs. 3 and 4, however, when the iron contents in the sphalerite are over 10%, it was found that the copper adsorption on sphalerites with the existence of dissolved oxygen was not so considerable in comparison with nitrogen gas. In the high alkaline solution containing copper ions, the higher the iron contents in sphalerite are, then the effects of dissolved oxygen in a solution are the more remarkable.

As shown in Figs. 2, 3, and 4, the log-log plot of the relationship between the adsorption rate of copper ions on the sphalerites and the agitation rate is characterized by a straight line.

$$\text{(Adsorption rate)} = \text{(Constant)} \times \text{(Agitation rate)}^{\iota} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

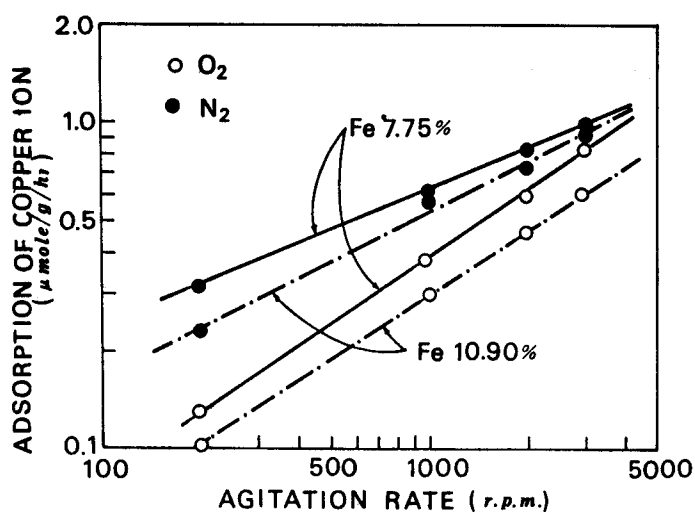The relations of Eq. (1) calculated from the results of Figs. 2, 3, and 4 are shown

Fig. 3. Effect of the agitation on the copper adsorption of
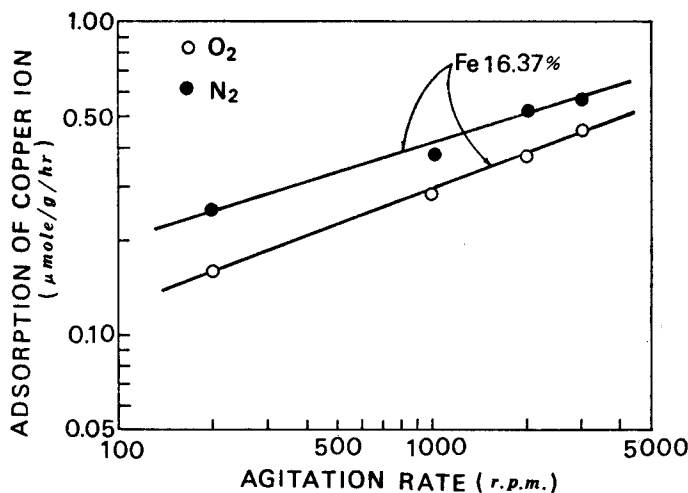sphalerites of Fe 7. 75% and 10. 90%.

Fig. 4. Effect of the agitation on the copper adsorption of
sphalerite of Fe 16.37%.

in Table 2. As shown in the adsorption rate equations of Table 2, when the iron
contents in the sphalerite are relatively low, the values of s in the case of nitrogen
gas are smaller than in the case of oxygen gas. It means that the copper adsorption
on sphalerites having low iron contents increases with the increase of the agitation rate,
even if the dissolved oxygen exists in a solution. With the increase of iron contents in
the sphalerite, however, the values of s in the cases of both oxygen and nitrogen gases
tend to get near. The values of s for sphalerites of Fe 16.37% are approximately
equal in the cases of both oxygen and nitrogen gases. From these results, it is recog-
nized that the effect of dissolved oxygen on the copper adsorption on sphalerites of
high iron contents is remarkable. Making a comparison among the copper adsorption
at the agitation rate of 2,000 rpm in Figs. 2, 3, and 4, their increase can be repre-
sented as follows Fe : 0.94% $<$ Fe 4.02% $<$ Fe 10.90% $<$ Fe 7.75% $<$ Fe 16.37%.
Then, the copper adsorptions at the agitation rate of 5,000 rpm were calculated by

Table 2. Relationship between the copper adsorption rate and agitation rate.

Fe (%)	O_2	N_2
0.94	$\Gamma = 3.68 \times 10^{-4} V^{0.880}$	$\Gamma = 1.07 \times 10^{-2} V^{0.518}$
4.01	$\Gamma = 3.28 \times 10^{-3} V^{0.693}$	$\Gamma = 1.14 \times 10^{-2} V^{0.558}$
7.75	$\Gamma = 4.13 \times 10^{-3} V^{0.654}$	$\Gamma = 3.78 \times 10^{-2} V^{0.406}$
10.90	$\Gamma = 3.68 \times 10^{-3} V^{0.636}$	$\Gamma = 1.76 \times 10^{-2} V^{0.487}$
16.37	$\Gamma = 2.25 \times 10^{-2} V^{0.371}$	$\Gamma = 4.65 \times 10^{-2} V^{0.319}$

Γ: COPPER ADSORPTION RATE $(mole/g/hr)$
V: AGITATION RATE $(r. p. m)$

extrapolating the results of Figs. 2, 3, and 4. Excepting a sphalerite sample of Fe 0.94%, they decreased in the following order: Fe 4.02%>Fe 7.75%>Fe 10 90%> Fe 16.37%. In the case of a strong agitation, it was recognized that the copper adsorption decreased with the increase of iron contents in the sphalerites, and that the effect of dissolved oxygen in the pulp was remarkable, especially in a high alkaline solution.

3.3. Kinetics on Copper Adsorption of Sphalerites of Various Iron Contents in Existence of Oxygen Gas.

According to A. M. Gaudin and his collaborator[6], they found that the formation of a CuS coating on sphalerites beyond the monolayer was controlled by ionic diffusion, and that the reaction rate should slow down once the surface was completely covered with one or two layers of CuS. The iron contents of the sphalerites used in their study were considerably low, and also any atmosphere such a oxygen gas was not taken into account. Accordingly, the present author carried out the kinetic considerations on the copper activation of sphalerites of various iron contents with and without oxygen gas. A series of comparative tests was done by using pyrrhotite from the Kawayama mine. This is the reason why the copper activation of pyrrhotite was remarkably effected by the dissolved oxygen in a high alkaline solution.

One gram of the 65~100 mesh sphalerite was added to 500 ml of a copper sulphate solution of 1×10^{-5} mole/l, which had been previously saturated with oxygen or nitrigen gas. Blowing a given gas at 100 ml/min of the flow rate, and agitating at 2,000 rpm, the copper adsorption on sphalerites of various iron contents was measured by the lapse of time under the fixed condition of pH 10.38.

The results obtained are given in Figs. 5~8. As can be seen in Figs. 5~8, the copper adsorption reactions of sphalerites of Fe 0.94% and 4.02% with oxygen and nitrogen gas, and Fe 7.75% with nitrogen gas are completely governed by a parabolic function. On the other hand, the relationship between the copper adsorption reaction of a sphalerite of Fe 7.75% with oxygen gas and time changed from a parabolic function to a exponential function. In sphalerites of over Fe 10.90%, it was found that the copper adsorption was shown by an exponential function of time both for oxygen and nitrogen gas. The copper adsorption reaction on pyrrhotite stopped completely with oxygen gas after about four hours. As C. H. G. Bushell[7] and C. S. Chang[8] had stated, it is surmised that the kinetics for the copper ion adsorption on pyrrhotite could be explained by the protective film theory.

From the above results, it was s found that the relationship between the copper adsorption and reaction time was governed by a parabolic function in the case of sphalerites below Fe 7.75%, and by an exponential function with the increase of iron
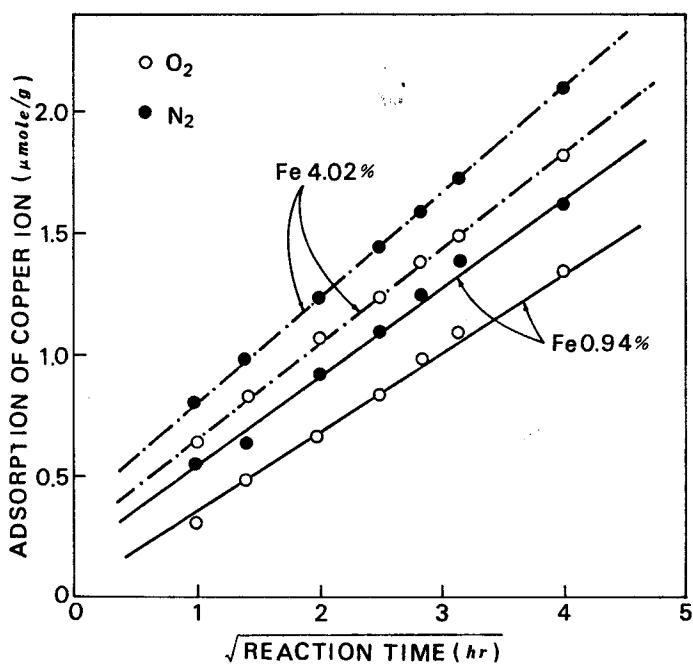
Fig. 5. Relationship between the copper adsorption and reaction time
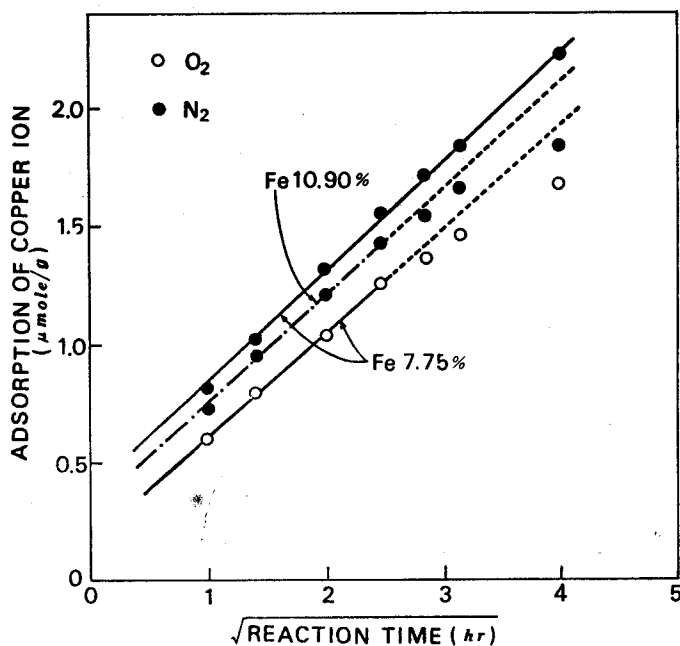in the case of sphalerites of Fe 0.94% and 4.02%.

Fig. 6. Relationship between the copper adsorption and reaction time
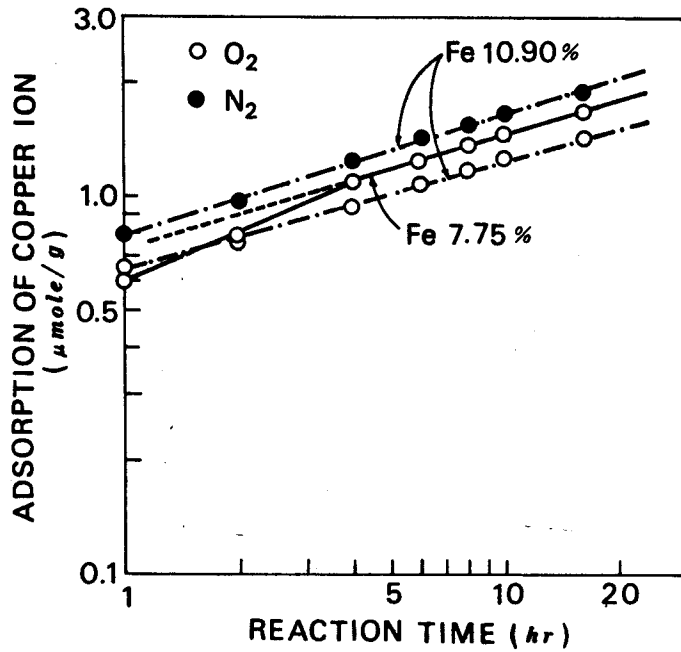in the case of sphalerites of Fe7.75% and 10.90%.

Fig. 7. Relationship between the copper adsorption and reaction rate in the case of sphalerites of Fe 7.75% and 10.90%.
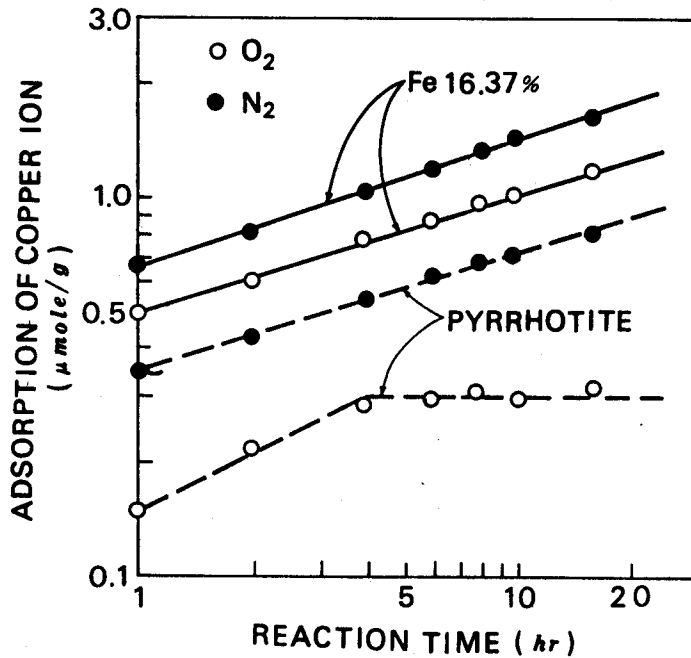

Fig. 8. Relationship between the copper adsorption and reaction time in the case of sphalerite of Fe 16.37% and pyrrhotite.

contents in the sphalerites.

Compared with the copper adsorption at the reaction time of 16 hr from the results of Figs. 5~8, it decreased in the following order (except the sphalerite sample of Fe 0.94%): Fe 4.02%>Fe 7.75%>Fe 10.90%>Fe 16.37%. If the mixture was strongly agitated to reach equilibrium after sufficient reaction time, it was recognized that the copper adsorption decreased with the increase of iron contents in the sphalerite.

It was done to represent the results of Figs. 5~8 quantitatively. In the case of sphalerite samples used in this experiment, the relationship between the copper adsorption and the reaction time is shown by either Eq. (2) or (3)

$$\Gamma_1^2 = k_1 t + k_2 \tag{2}$$

$$\Gamma_2 = k_3 t^n \tag{3}$$

where Γ_1 and Γ_2 are the copper adsorption (mole/g), t is the reaction time (hr), n and k_1, k_2, k_3 are the constants which are obtained by the experiment. Calculating the relations of Eq. (2) and (3) from Figs. 5~8, the results obtained are shown in Table 3. As can be seen in Table 3, the experimental results of Figs. 5~8 were quantitatively represented to further clarify the above stated.

Table 3. Rate equations of copper adsorption on various mineral samples.

Fe(%)	N₂	O₂
0.94	$\Gamma = 0.367\ t^{1/2} + 0.17$	$\Gamma = 0.320\ t^{1/2} + 0.04$
4.02	$\Gamma = 0.433\ t^{1/2} + 0.36$	$\Gamma = 0.387\ t^{1/2} + 0.27$
7.75	$\Gamma = 0.493\ t^{1/2} + 0.38$	$\Gamma = 0.440\ t^{1/2} + 0.17 (1 \leq t \leq 6)$
		$\Gamma = 0.71\ t^{0.311} (6 \leq t)$
10.90	$\Gamma = 0.79\ t^{0.306}$	$\Gamma = 0.64\ t^{0.282}$
16.37	$\Gamma = 0.66\ t^{0.326}$	$\Gamma = 0.49\ t^{0.317}$
57.14 (PYRRHOTITF)	$\Gamma = 0.35\ t^{0.293}$	$\Gamma = 0.15\ t^{0.273} (1 \leq t \leq 4)$
		$\Gamma = 0.30 (4 \leq t)$

Γ: ADSORPTION OF COPPER ION(mole/g)
t: REACTION TIME (hr)

On the basis of the results of Figs. 5~8, the lowering percentage of copper adsorption in the case of existence of dissolved oxygen was calculated, by assuming that the copper adsorption of 16 hr of reaction time with nitrogen gas is 100%. The results obtained are given in Fig. 9. As shown in Fig. 9, the effect of dissolved oxygen in the solution was remarkable, because the lowering of copper adsorption was considerable with the increase of iron contents in the sphalerites by the dissolved oxygen in the solution. The lowering of copper adsorption on pyrrhotite was about 60%. In
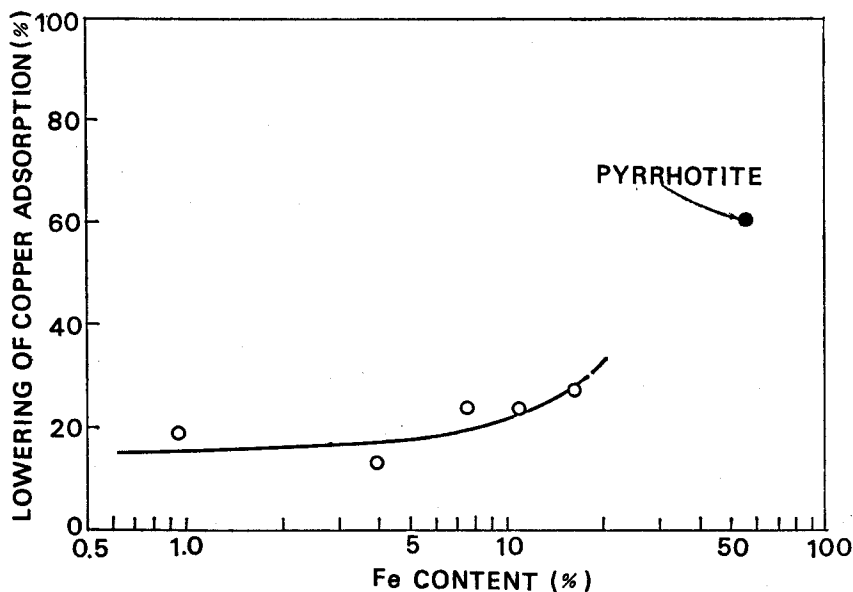
Fig. 9. Effect of the iron contents in mineral samples on the
lowering of copper adsorption.

this case, the effect of dissolved oxygen in the solution was the most remarkable.

From the above results, it may be considered that the dissolved oxygen in the solution is one of the important factors for the copper activation of sphalerites as well as pyrrhotite.

4. Conclusions

In this study, the effect of dissolved oxygen in the solution on the copper adsorption of sphalerites having various iron contents was kinetically examined. The results obtained from this study are summarized as follows

(1)   The copper adsorption on sphalerites was maximum at about pH 6~7 without the agitation, and decreased in both the acid and alkaline regions. It was recognized that the pH dependence for the adsorption of copper ions on all sphalerites used in this experiment was remarkable, and that the copper adsorption increased with the increase of iron contents in the sphalerites.

(2)   The effect of agitation on the copper adsorption of sphalerites of various iron contents was examined. Under the condition of strong agitation, it was found that the copper adsorption decreased with the increase of iron contents in the sphalerites, and that the effect of dissolved oxygen in the solution was remarkable in a high alkaline solution containing copper ions.

(3)   By measuring the copper adsorption on shalerites with a lapse of time, the

kinetics for the copper adsorption on sphalerites of various iron contents were examined. From the results obtained, it was found that the reaction rate of the copper ion adsorption on sphalerites changed from the rate of a parabolic function to the rate of an exponential function with the increase of iron contents in the sphalerite. As can be seen by the results of this study, it may be considered that the dissolved oxygen in the solution is also one of the important factors for the copper activation of sphalerite.

References

1) S. Mukai and Y. Nakahiro: Journal of the Mining and Metallurgical Institute of Japan, Vol. 85, No. 970, 1969, p. 77.: The Memoirs of the Faculty of Engineering, Kyoto University, Vol. XL, Part 3, 1978, p. 101.
2) G. Kullerud: Norsk Tidsskr, Vol. 32, 1953, p. 61.
3) H. Mino: Journal of the Mining and Metallurgical Institute of Japan, Vol. 73, No. 824, 1957, p. 93.
4) M. Ishibashi and T. Fujinaga: "Polarography", Maruzen Co. Ltd., Tokyo, Japan, p. 398.
5) S. Mukai and Y. Nakahiro: ibid. 1.
6) A. M. Gaudin, D. W. Fuerstenau, and G. W. Mao: Trans. AIME, Vol. 214, 1959, p. 431.
7) C. H. G. Bushell, C. J. Krauss, and G. Brown: Can. Min. Met. Bull., March 1961, p. 244
8) C. S. Chang, S. R. B. Cooke, and I. Iwasaki: Min. Eng., Feb. 1954, p. 209.