

Study on Deactivation of Sphalerite with Sulphuric Acid and Ferric Ion Solutions

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Abstract

The separation of Cu/Zn ores in the flotation treatment of complex sulphide ores is very difficult because of copper activation. Therefore, the deactivation of copper-activated sphalerite is one of the most important subjects in the flotation operation of complex sulphide ores.

In this study, the deactivation of copper-activated sphalerite has been investigated in a series of laboratory experiments.

Firstly, the effects of sulphuric acid and ferric ions in the presence of sulphuric acid on the deactivation of copper-activated sphalerite were examined from the flotation tests by the Hallimond tube. From the results obtained, it was found that the deactivation of copper-activated sphalerite could be attained to some degree by a 3~5 vol. % H_2SO_4 solution, and could be attained very well by a 500~1,000 mg/l Fe^{+++} solution containing H_2SO_4 . In this case, oxygen gas accelerated the deactivation of the sphalerite in the treatment of both the above solutions. Temperature was also one of the important factors for the deactivation.

Secondly, the dissolution of the copper-activated film formed on the sphalerite was investigated. From the results obtained, it was found that copper-activated film could be dissolved completely by the Fe^{+++} solution containing H_2SO_4 , and could be dissolved to some degree by the H_2SO_4 solution.

The dissolution rate of the activated film was measured as a function of the concentration of Fe^{+++} and H_2SO_4 and of the temperature. The dissolution rate is shown by a linear equation.

Using a flotation machine, a series of differential flotation tests of Cu/Zn sulphide ores was carried out. From the results obtained, it was confirmed that the flotation separation of Cu/Zn sulphide ores was successful by the deactivation treatment for the Cu/Zn sulphide ores.

1. Introduction

Up to now, one of the most difficult subjects in the flotation operation of complex sulphide ores has been the differential flotation of Cu/Zn sulphide ores. This is because

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both sulphide ores show similar floatability on account of the copper activation for sphalerite. In order to solve this problem, it is necessary to establish a method of preventing copper activation for sphalerite by eliminating copper ions from the flotation pulp, or by deactivating the copper-activated film on the sphalerite surface.

The effect of sodium sulphide for preventing copper activation for sphalerite has been reported in a previous paper.¹⁾ On the other hand, sodium cyanide has been shown to be effective as a deactivator of copper-activated sphalerite by A. M. Gaudin and his colleagues.²⁾ While cyanide ion shows a considerably depressing effect for some sulphide minerals, however, it is doubtful whether sodium cyanide can be used as a deactivator on a Cu/Zn differential flotation or not. Accordingly, the author tried in this paper to examine the deactivation of copper-activated sphalerite with acid and ferric ion solutions. Although this method has been considered by V. A. Glembotsky and M. M. Sorokin,³⁾ the details on treating conditions and experimental results were not available to us. In this study, more detailed experiments were carried out in order to confirm the effect of the deactivation of copper-activated sphalerite with acid and ferric ion solutions. Furthermore, the additional effect of blowing oxygen gas into acid and ferric ion solutions was also examined.

2. Preparation of Mineral Samples

Sphalerite from the Toyoha mine in the Hokkaido district and chalcopyrite from the Kishu mine in Wakayama prefecture, Japan, were used in this experiment.

A high grade sample of each of the above minerals was selected and crushed. Then, pure mineral particles 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.

3. Deactivation of Sphalerite with Acid and Ferric Ion Solutions

In this study, the effects of sulphuric acid, ferric ion in the presence of sulphuric acid and the treating temperature on the deactivation of copper-activated sphalerite were examined from the flotation tests by the Hallimond tube.

3.1. Deactivation of Copper-Activated Sphalerite with Sulphuric Acid.

i) Effect of Sulphuric Acid Concentration.

In a series of tests, one gram of 65~100 mesh sphalerite was weighed and then sphalerite was copper-activated by treatment as follows. One gram of sphalerite was

slowly agitated in a solution of 50 ml containing copper sulphate of $\text{Cu}^{++} 1 \times 10^{-6}$ mole/l. The solution was kept in a thermostat at 25°C for one hour. The supernatant of mixture solution was removed by the decantation method, and then the copper-activated sphalerite sample was washed thoroughly by distilled water in order to eliminate excess copper ions and metal ions dissolved into the solution. After the copper-activated sphalerite was prepared in this way, a solution of 50 ml containing known amounts of sulphuric acid was added to the copper-activated sphalerite. The mixture solution was kept in the thermostat at 40°C for one hour. The supernatant of mixture solution was removed by the decantation method, and then the sample was washed thoroughly by distilled water. After being treated as above, a series of flotation tests was carried out. The concentration of sulphuric acid in this study is indicated by vol.% unless otherwise noted.

The deactivated sphalerite sample was transferred to the Hallimond tube, and then was conditioned for three minutes in a potassium ethyl xanthate solution of about 150 ml having various pH values. Flotation was carried out by blowing nitrogen gas into the Hallimond tube for six minutes. The float and sink were dried and weighed. The pH adjustment was carried out by using HCl or NaOH. The concentration of potassium ethyl xanthate, used in a series of tests, was constant at 25 mg/l.

The results obtained are as shown in Figs. 1 and 2. Fig. 1 shows the result without oxygen gas. Fig. 2 shows the result with oxygen gas. The oxygen gas used in this study was purified through silica gel and NaOH. The flow rate of oxygen gas was constant at 0.5 l/min. As shown in Fig. 1, the floatability of copper-activated sphalerite

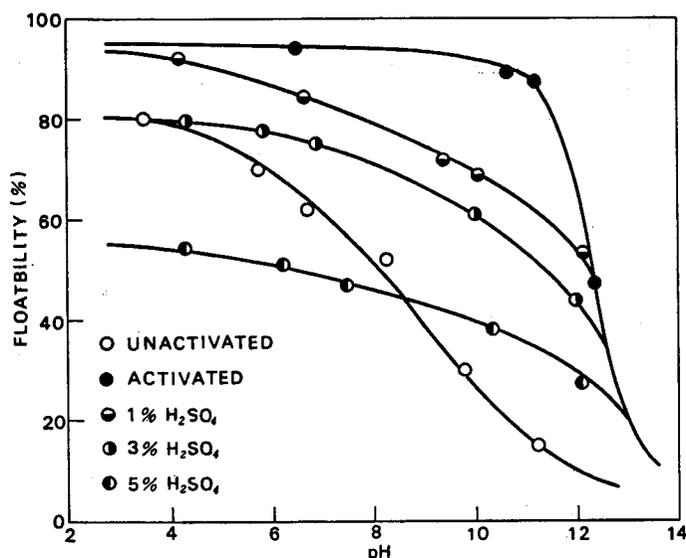


Fig. 1. Effect of sulphuric acid concentrations on the deactivation of the copper-activated sphalerite. (without oxygen gas)

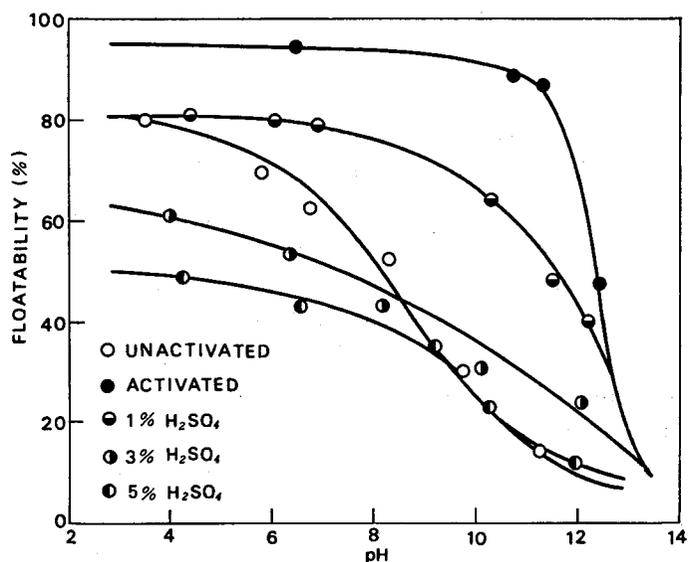


Fig. 2. Effect of sulphuric acid concentrations on the deactivation of the copper-activated sphalerite. (with oxygen gas)

decreased with the increase of sulphuric acid concentration, and then it approached the floatability of unactivated sphalerite. As shown in Fig. 2, however, the floatability of copper-activated sphalerite decreased more and more with oxygen gas. In this case, copper-activated sphalerite was treated for deactivation with sulphuric acid of over 3%

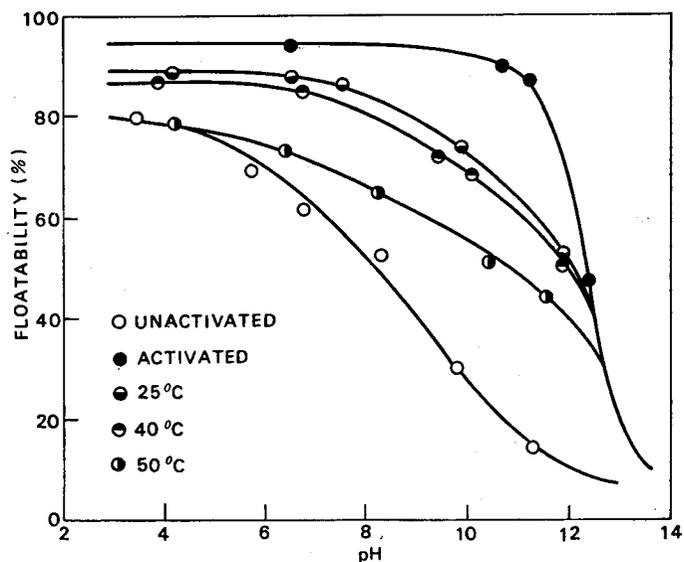


Fig. 3. Effect of treating temperature on the deactivation of the copper-activated sphalerite with sulphuric acid of 1%. (without oxygen gas)

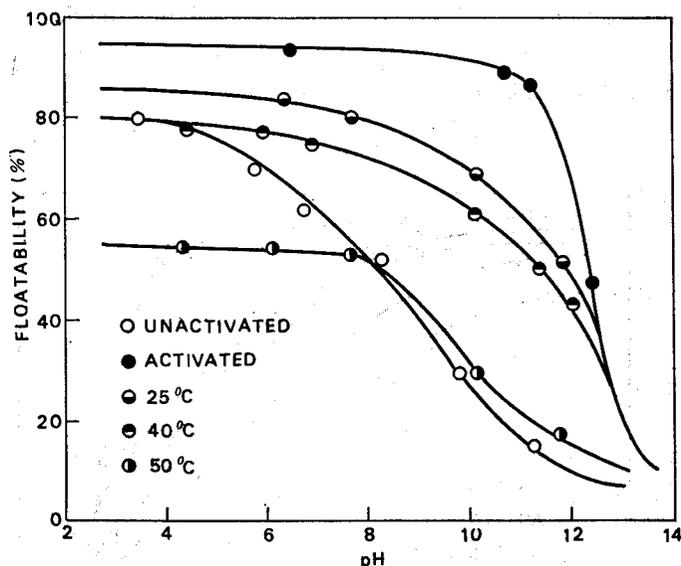


Fig. 4. Effect of treating temperature on the deactivation of the copper-activated sphalerite with sulphuric acid of 3%. (without oxygen gas)

and oxygen gas. From the above results, it was recognized that blowing gas in the treatment of deactivation with sulphuric acid had a remarkable effect.

ii) Effect of Treating Temperature.

Copper-activated sphalerite was prepared by the same treatment as above. The treatment for deactivation was carried out by varying the treating temperatures with sulphuric acid of 1% and 3%. Figs. 3 and 4 show the results obtained. Fig. 3 shows the result with sulphuric acid of 1%, and Fig. 4 with sulphuric acid of 3%. As shown in Fig. 3, in the case of the sulphuric acid concentration of 1%, the floatability of deactivated sphalerite decreased slightly with the increase of the treating temperature. In this case, however, the effect of increasing the treating temperature was not so remarkable for the elimination of the copper-activated film on the sphalerite surface. As shown in Fig. 4, in the case of the sulphuric acid concentration of 3%, the floatability curve with the deactivating treatment at 50°C coincided with that of unactivated sphalerite. From these results, it was surmised that the deactivating treatment with sulphuric acid was effective to some extent.

3.2. Deactivation of Copper-Activated Sphalerite with both Sulphuric Acid and Ferric Ion.

i) Effect of Ferric Ion Concentration.

The copper-activated sphalerite was prepared by the treatment as mentioned above, and it was slowly agitated in a solution of 50 ml containing ferric ions of a given concen-

tration in the presence of sulphuric acid of 0.4%. The mixture solution was kept in the thermostat at 40°C for one hour. The supernatant of mixture solution was removed by the decantation method, and then the deactivated sphalerite was washed thoroughly by distilled water. A series of flotation tests was carried out as mentioned above. Ferric

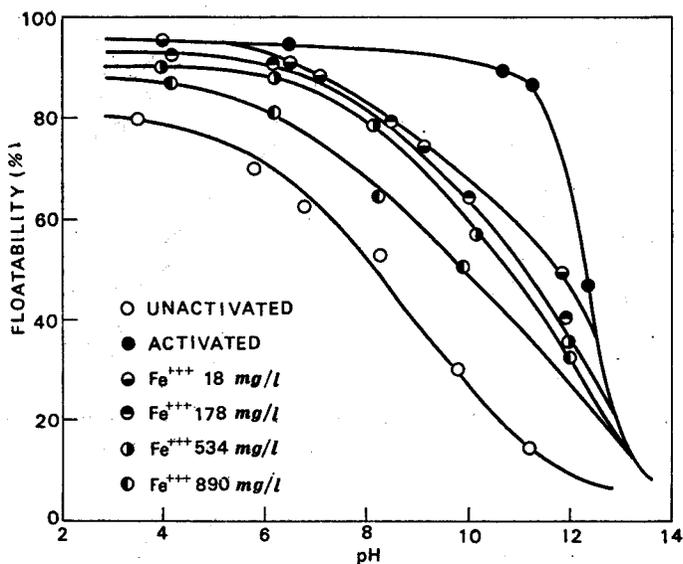


Fig. 5. Effect of ferric ion concentrations on the deactivation of the copper-activated sphalerite. (without oxygen gas)

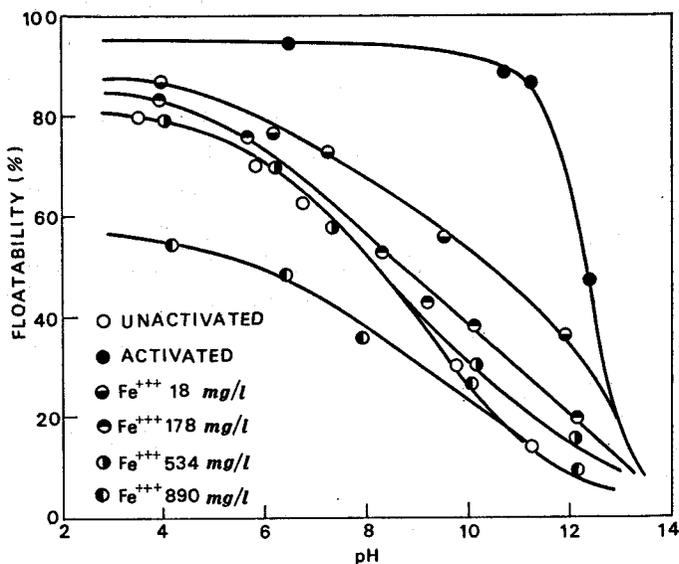


Fig. 6. Effect of ferric ion concentrations on the deactivation of the copper-activated sphalerite. (with oxygen gas)

sulphate, which was chemically pure, was used as the ferric ion solution for these experiments. The concentration of ferric ions was decided by titration using potassium permanganate.

The results obtained are given in Figs. 5 and 6. Fig. 5 shows the result without oxygen gas and Fig. 6 with oxygen gas. As shown in Fig. 5, the floatability of deactivated sphalerite decreased with the increase of ferric ion concentration and approached that of unactivated sphalerite. As shown in Fig. 6, in the case where oxygen gas was blown into the solution, it was recognized that copper-activated sphalerite was completely deactivated by adding ferric ions of over 534 mg/l in the presence of oxygen gas.

From the above results, the effect of blowing oxygen gas into sulphuric acid and ferric ions in the presence of sulphuric acid was considerable. In particular, in the case where ferric ions were used together with sulphuric acid in the presence of oxygen gas, the addition of sulphuric acid decreased about one tenth less than in the case of the deactivating treatment by only sulphuric acid.

ii) Effect of Treating Temperature.

After preparing the copper-activated sphalerite sample, it was slowly agitated in a solution of 50 ml containing ferric ions of 534 mg/l and 890 mg/l in the presence of sulphuric acid of 0.4%, blowing oxygen gas during the deactivating treatment. The mixture solution was kept in the thermostat by varying the treating temperature for one hour. The results obtained are given in Figs. 7 and 8. Fig. 7 shows the result with the addition of Fe^{+++} 534 mg/l, and Fig. 8 with the addition of Fe^{+++} 890 mg/l. As shown

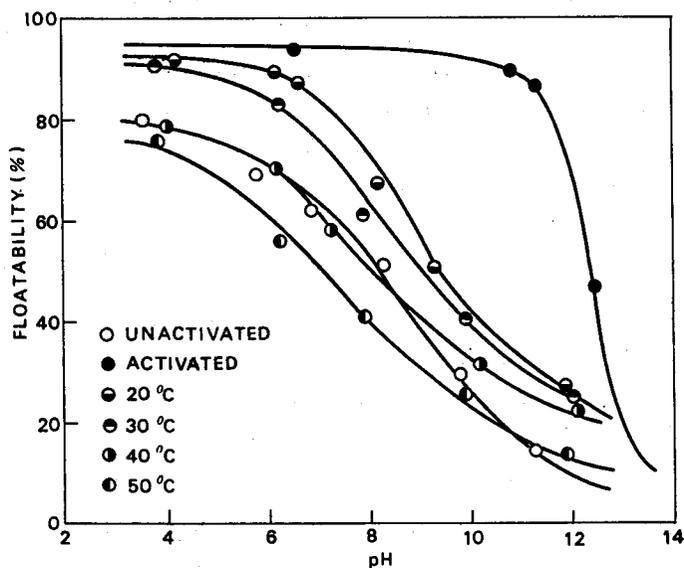


Fig. 7. Effect of treating temperature on the deactivation of the copper-activated sphalerite with ferric ions of 534 mg/l. (with oxygen gas)

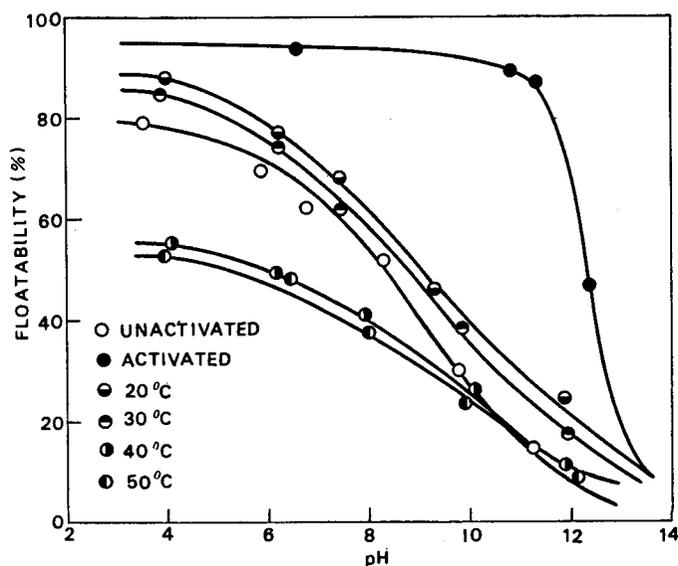


Fig. 8. Effect of treating temperature on the deactivation of the copper-activated sphalerite with ferric ions of 890 mg/l. (with oxygen gas)

in Figs. 7 and 8, the effect of deactivation on copper-activated sphalerite was not recognized because the sphalerite floated in any addition of ferric ions under 30°C. In the addition of ferric ions 534 mg/l over 40°C and in the addition of ferric ions 890 mg/l over 30°C, the floatability curve of the deactivated sphalerite coincided with that of the unactivated sphalerite. In such experimental conditions, it was recognized that copper-activated sphalerite was completely deactivated with ferric ions containing sulphuric acid.

From the above results, it was obvious that the treating temperature was an important factor. Although the degree of deactivation on copper-activated sphalerite was incomplete in the treating temperature under 30°C, it was recognized that the effect of deactivation was remarkable with the increase of the treating temperature.

4. Dissolution of Copper-Activated Film on Sphalerite Surface

In the previous sections, the deactivation of copper-activated sphalerite with sulphuric acid or ferric ions in the presence of sulphuric acid was considered from the results of flotation tests. In order to indicate the previous results even more quantitatively, the amounts of dissolved copper ions were measured by dissolution tests after deactivating the copper-activated sphalerite with sulphuric acid and ferric ions.

4.1. Dissolution of Copper-Activated Film on Sphalerite Surface.

The preparation of the used sample was as follows: a 65~100 mesh fraction was ground in an agate mortar. The ground sample of sphalerite was sieved by a 200 mesh

Tyler Standard Screen and a -200 mesh fraction prepared. The sample obtained was washed repeatedly in pure water to eliminate fine particles under 10 micron, and was used for the experiment after being dried in the vacuum desiccator.

The experimental procedure was as follows: one gram of -200 mesh sphalerite sample was copper-activated with a copper ion solution of 1×10^{-4} mole/l by the treatment mentioned before. After preparing the copper-activated sphalerite, a solution of 50 ml of sulphuric acid or ferric ions containing sulphuric acid was added to the copper-activated sphalerite. The mixture solution was kept in the thermostat at 40°C for one hour. Then, the mixture solution was filtered through filter paper in order to eliminate the sphalerite sample in the mixture solution. The copper ion concentrations in the filtrate were measured by the Jarrell-Ash atomic adsorption spectrometer. The amounts of the desorption were determined by making 100% the amounts of copper ions adsorbed initially. Blank tests were also carried out in order to detect the amounts of leached copper ions in the case where there was no treatment of copper ions for sphalerite.

The results obtained are given in Figs. 9 and 10. Fig. 9 shows the result without the blowing of oxygen gas, and Fig. 10 with the blowing of oxygen gas. In these experiments, the flow rate of oxygen gas was 0.5 l/min. As shown in Fig. 9, in the case where only sulphuric acid was used, the copper-activated film, which was adsorbed on the sphalerite surface, was substantially dissolved with a ferric ion solution even in a sulphuric acid concentration of 0.2%, and a desorption of about 55% was shown in a sulphuric acid concentration of 0.4%. It is worth noting that the copper-activated film on

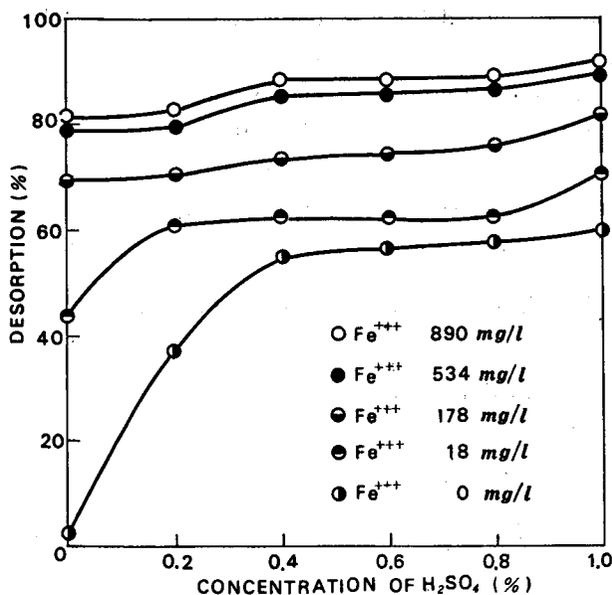


Fig. 9. Desorption of copper-activated film on the sphalerite surface with sulphuric acid and ferric ions. (without oxygen gas)

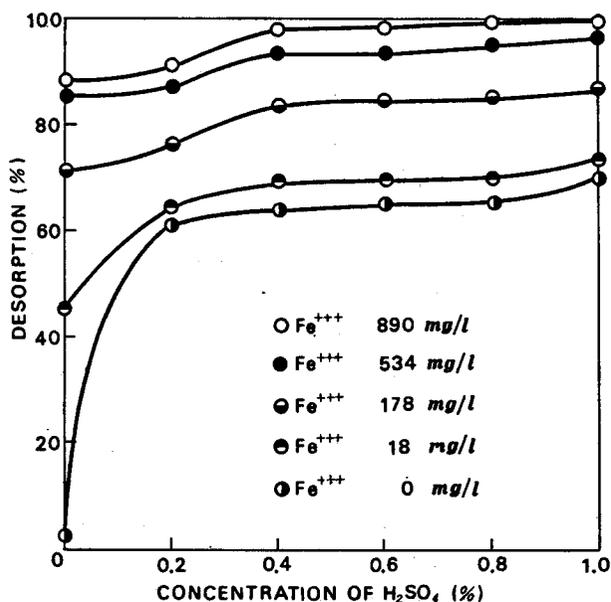


Fig. 10. Desorption of copper-activated film on the sphalerite surface with sulphuric acid and ferric ions. (with oxygen gas)

the sphalerite surface was dissolved to some extent with a diluted sulphuric acid solution. Only the deactivating treatment with sulphuric acid was not sufficient for the complete removal of the copper-activated film on the sphalerite surface. On the other hand, the removal of the copper-activated film was considerable in the case where ferric ions were added to sulphuric acid, and the desorption of the copper-activated film increased with the increase of ferric ion concentration. As shown in Fig. 10, the effect on the removal of the copper-activated film was considerable in the case where oxygen gas was blown into the solution. In this case, a desorption of over 95% was obtained under the conditions of Fe⁺⁺⁺ 890 mg/l and H₂SO₄ over 0.4%. Under these conditions, it was confirmed that the dissolution of the copper-activated film was almost complete.

4.2. Effect of Treating Temperature on Dissolution Rate of Copper-Activated Film.

Arrhenius found experimentally the following relation on the temperature variation of the reaction rate.⁴⁾

$$d \ln k / dT = E_A / RT^2 \quad (1)$$

where T is the absolute temperature, R is the gas constant, E_A is the activation energy, and k is the reaction rate constant. In this study, it was considered whether the relationship of the above equation was realized or not.

The measurement of the dissolution rate was carried out by varying the concent-

rations of ferric ions and treating temperatures under the fixed concentration of H_2SO_4 0.4%. The adsorption of the copper-activated film was plotted as a function of the treating time.

If the reaction rate is proportional to the n th power of a type of chemical species $[A]$ of the reactant, the general equation is as follows:

$$-d[A]/dt = k_n[A]^n \quad (2)$$

where k_n is the proportional constant which is independent of the concentration of the species of the reactant. When the amount of $[A]$ is a initially, and the amount of reaction is x in the arbitrary time t ,

$$-d[A]/dt = k_n(a-x)^n \quad (3)$$

Integrating Eq. (3) under the initial condition of $[A]$ in $t=0$ in the case of $n=1$ and $[A]=a-x$, we can get Eq. (4).

$$kt = \ln \left(\frac{a}{a-x} \right) \quad (4)$$

The results obtained are given in Fig. 11. Fig. 11 shows the results with the addition of Fe^{+++} 534 mg/l. As shown in Fig. 11, the dissolution reactions are composed of two stages. One stage is a very fast reaction in which the dissolution will finish within about 30 minutes, and the other is a slow reaction which continues until the reaction system reaches the equilibrium. From the results shown in Fig. 11, it was recognized

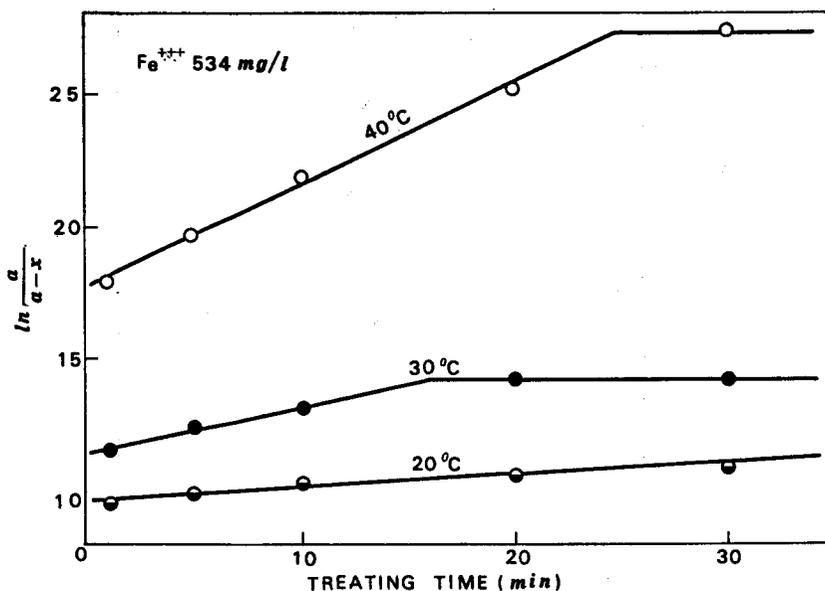


Fig. 11. Relationship between $\ln \left(\frac{a}{a-x} \right)$ and time t .

that the relationship between $\ln\left(\frac{a}{a-x}\right)$ and time t conformed to Eq. (4). From the above results, it was recognized that the dissolution of the copper-activated film on the sphalerite surface with sulphuric acid and ferric ions was shown by the 1st order reaction. Therefore, it is considered that the dissolution rate is accelerated remarkably by agitating the mixture solution, because the dissolution of copper-activated film is controlled by the diffusion.

Next, the same experiment as mentioned above was carried out by varying the concentrations of ferric ions. From the experimental results, the relationship between the rate constant and temperature was decided. The results obtained are given in Fig. 12. As shown in Fig. 12, it was recognized that Fig. 12 satisfied Eq. (1), and the elevation of the temperature considerably increased the dissolution rate.

If the dissolution rate is assumed to be the m factor, m is as follows:

$$m = k_{80+10} / k_{80} \quad (5)$$

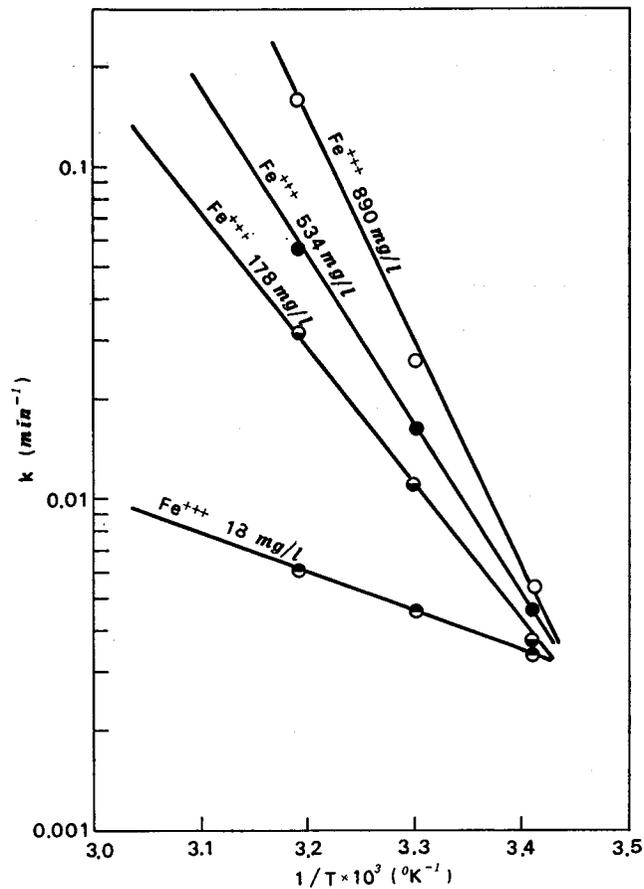


Fig. 12. Relationship between the reaction rate constant and the treating temperature.

where k_{θ_0} is the rate constant in any standard temperature $\theta_0^\circ\text{C}$, and k_{θ_0+10} is the rate constant in $(\theta_0+10)^\circ\text{C}$. Calculating the values of m for ferric ion concentrations 18, 178, 534 and 890 mg/l by applying Eq. (5) from the results of Fig. 12, we obtained 1.35, 2.75, 3.63 and 5.37 respectively. When the concentration of ferric ions is low, such as 18 mg/l, the dissolution rate is about 1.4 factors against the temperature rise of 10°C , and it is a small value relatively. However, the more the concentrations of ferric ions increase, the value of m becomes larger. It was recognized that the dissolution rate reached about 5.4 factors from these experimental results in the case of the ferric ion concentrations of 890 mg/l.

From the above results, it was concluded that the dissolution reaction of copper-activated film with a ferric ion solution depended on the temperature and ferric ion concentrations, and that the dissolution rate was shown by the 1st order equation.

5. Effect of Deactivation Treatment in Differential Flotation of Copper-Activated Cu/Zn Ores

For the copper-activated Cu/Zn ores, in which the differential flotation is very difficult, a series of flotation tests was carried out in order to confirm the degree of the Cu/Zn separation, using the deactivating treatment with ferric ions and sulphuric acid.

The experimental procedure was as follows: five grams of sphalerite and chalcopyrite were weighed respectively and then both mineral samples were activated with a solution of 250 ml containing copper sulphate of $\text{Cu}^{++} 1 \times 10^{-6}$ mole/l at 25°C for one hour. After activating the samples in this way, the supernatant of mixture solution was removed by filtration, and then the copper-activated mineral samples were washed thoroughly by distilled water. Next, the copper-activated mineral samples were treated by adding a solution of 250 ml containing potassium ethyl xanthate of 25 mg/l at 25°C for 30 minutes. The mineral samples treated by potassium ethyl xanthate were filtered and washed in order to eliminate excess potassium ethyl xanthate in the presence of the mixture solution. A solution of 250 ml containing a known concentration of sulphuric acid and ferric ions was added to the Cu/Zn mineral samples treated as mentioned above. The mixture solution was kept in the thermostat at 40°C for one hour, blowing oxygen gas at the flow rate of 0.5 l/min. Then, the samples were washed thoroughly in distilled water. A series of flotation tests was carried out by a 250 ml MS type flotation test machine. Distilled water of 225 ml and mineral samples were added to the flotation cell, and then the given amounts of sodium cyanide and zinc sulphate were added. After agitating for five minutes, the pH of the flotation pulp was adjusted by NaOH or HCl. Next, a given amount of potassium ethyl xanthate and one drop of pine oil were added to the flotation pulp, and the conditioning was carried out for one minute. After the froth was skimmed for five minutes, the float and sink products were dried

weighed. The flotation conditions are as follows: potassium ethyl xanthate, 25 mg/l; pine oil, 28 mg/l; NaCN, 40 mg/l; ZnSO₄, 200 mg/l.

First, a series of flotation tests without any deactivating treatment was carried out on the copper-activated and -unactivated mineral samples in order to compare results with and without a deactivating treatment. The results obtained are given in Fig. 13.

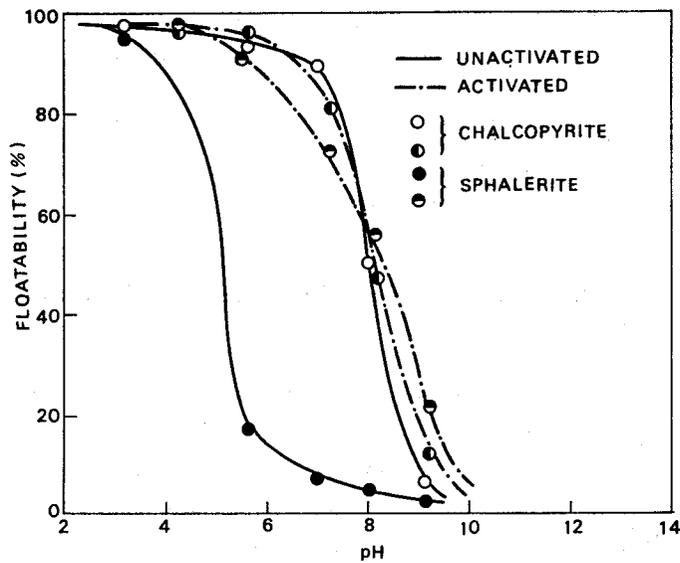


Fig. 13. Effect of copper ions on the copper and zinc recoveries of the float product in the Cu/Zn differential flotation.

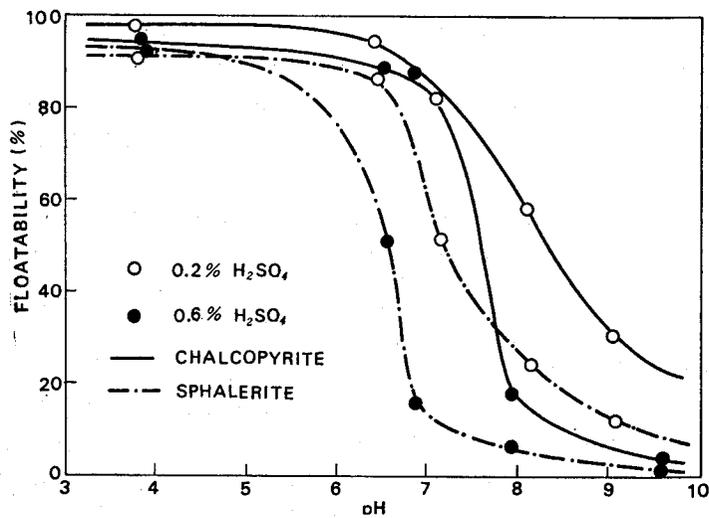


Fig. 14. Effect of deactivating treatment with sulphuric acid and ferric ions on the copper and zinc recoveries of the float product.

As shown in Fig. 13, the unactivated Cu/Zn mineral samples were successfully separated at pH 6~8, and the copper recovery in the float product was about 90% at pH 7.0. The zinc recovery was about 92%. However, the copper-activated sphalerite showed the same flotation behaviour as chalcopyrite at all pH values, and the separation of both minerals was impossible.

Secondly, a series of flotation tests for the Cu/Zn flotation separation was carried out in the case where the deactivating treatment was carried out by varying sulphuric acid concentrations under the fixed condition of Fe^{+++} 890 mg/l. The results obtained are given in Fig. 14. As shown in Fig. 14, the pH values for the Cu/Zn flotation separation were about 6.5~7.5, though the separation pH values were relatively narrow. From the results of Fig. 14, the recoveries of Cu and Zn in the float products were calculated. Fig. 15 shows the results obtained. As shown in Fig. 15, the results of the Cu/Zn flotation separation were successful, and the copper recovery in the float product was about 85%. The zinc recovery in the sink product was about 86%. From the above results, it was recognized that the effect of a deactivating treatment with sulphuric acid and ferric ions by blowing oxygen gas was remarkable.

Fig. 16 shows the results of the Cu/Zn flotation separation in the case where the deactivating treatment was carried out with sulphuric acid of 5% by blowing oxygen gas. As shown in Fig. 16, the deactivating treatment by using only sulphuric acid was not effective in comparison with the deactivating treatment with ferric ions.

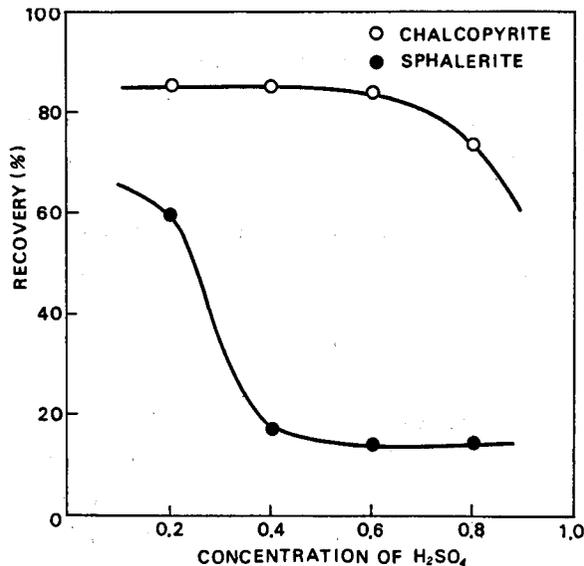


Fig. 15. Relationship between sulphuric acid concentrations in the deactivating treatment with ferric ions in the presence of sulphuric acid and the copper and zinc recoveries of float product at pH 7.

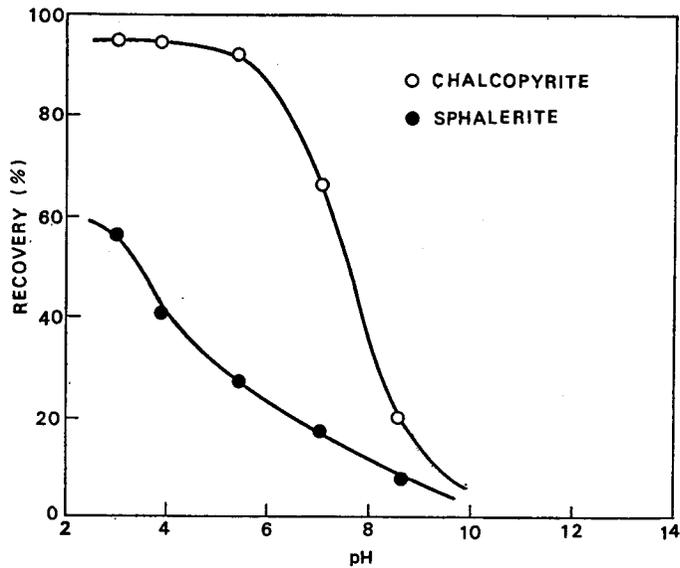


Fig. 16. Effect of deactivating treatment with sulphuric acid on the copper and zinc recoveries of float product.

From the above results, it was recognized that the copper-activated sphalerite was deactivated by the deactivating treatment with sulphuric acid and ferric ions blowing oxygen gas, and that the differential flotation of Cu/Zn minerals was successfully carried out without changing the floatability of chalcopyrite.

6. Conclusions

The effects of sulphuric acid and ferric ions in the presence of sulphuric acid on the deactivation of copper-activated sphalerite were examined from the flotation tests by the Hallimond tube and from the dissolution tests. Further, in order to overcome the difficulties of the Cu/Zn differential flotation resulting from the copper ions, the separation conditions for the differential flotation were considered by treating the deactivation with both solutions.

The results of this study are summarized as follows:

- 1) The effects of concentrations of sulphuric acid and ferric ions were examined for the elimination of copper-activated film on a sphalerite surface from the floatability measurement by the Hallimond tube. In every case, the effect of copper-activation on sphalerite disappeared completely with the increase of the concentrations of both solutions. When sulphuric acid was used simultaneously with a ferric ion solution, however, the addition of sulphuric acid decreased about one tenth less than in the case of the deactivating treatment using only sulphuric acid. In any deactivating treatment with sulphuric acid or ferric ions in the presence of sulphuric acid, it was recognized that the

effect of blowing oxygen gas into the solutions was effective.

2) From the results examined by the floatability measurement using the Hallimond tube on the effect of the treating temperature in the deactivating treatment with sulphuric acid or ferric ions in the presence of sulphuric acid, it was obvious that the treating temperature was an important factor. Although the degree of deactivation on copper-activated sphalerite was incomplete in the treating temperature under 30°C, it was recognized that the effect of deactivation was remarkable with the increase of the treating temperature over 30°C.

3) In order to indicate the above results even more quantitatively, the amounts of dissolved copper ions were measured by dissolution tests after deactivating the copper-activated sphalerite with sulphuric acid and ferric ions. In this case, the effect of blowing oxygen gas into the solutions was effective, and a desorption of over 95% was obtained under the conditions of Fe^{+++} 890 mg/l and H_2SO_4 over 0.4%. Under these conditions, it was confirmed that the dissolution of copper-activated film was almost complete.

4) From the results examined on the effect of the treating temperature on the dissolution rate of copper-activated film, the dependency of the treating temperature and ferric ion concentration on the dissolution reaction was considerable, and the dissolution rate was shown by the 1st order equation.

5) A series of flotation tests was carried out in order to confirm the degree of separation for the copper-activated Cu/Zn ores, using the deactivating treatment of sulphuric acid and ferric ions. In all deactivating treatments with sulphuric acid and ferric ions containing sulphuric acid by blowing oxygen gas, the effect of copper activation on sphalerite was nullified by the deactivating treatment with both solutions. When Cu/Zn ores were simultaneously treated with the deactivating treatment, it was recognized that the differential flotation of Cu/Zn ores was successfully carried out without changing the floatability of chalcopyrite.

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