Effect of Sodium Sulphide on the Prevention of Copper Activation for Sphalerite

By

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Abstract

The effect of sodium sulphide on the prevention of copper activation for sphalerite was studied.

The adsorption of copper ions on sphalerite was measured in a solution containing copper ions and sodium sulphide by varying the pH value of the solution. From the results obtained, it was recognized that the adsorption of copper ions was prevented completely in an alkaline solution containing sodium sulphide.

When sodium cyanide was used as a depressant, the effect of sodium sulphide on the prevention of copper activation was investigated. Up to a certain amount of sodium cyanide, the floatability of sphalerite increases with the increase of sodium cyanide. It was confirmed that this phenomenon was caused by coating copper sulphide particles or copper complexes precipitated by sodium sulphide on the sphalerite surface. However, by increasing the concentration of sodium cyanide to over 30 mg/l and by the addition of sodium sulphide, it was seen that the depressing effect of sodium cyanide was considerable.

In the case where sulphurous acid was used as a depressant, the floatability of sphalerite did not decrease at the low pH value, and colloidal sulphur was formed by the decomposition of sodium sulphide. However, with the increase of the pH value and the amounts of sulphurous acid, the depressing effect of sulphurous acid in the presence of sodium sulphide was most marked.

Consequently, it may be considered that copper activation for sphalerite is prevented completely when using sodium sulphide.

1. Introduction

The ores containing many kinds of sulphide minerals, such as complex sulphide ores, have an exceptional tendency to be oxidized and lead to the formation of more soluble salts during the oxidation. The various metallic ions originate from these soluble salts. Among these ions, the copper ions in particular have a notably unfavourable influence on the flotation property of sulphide minerals. As a result, it is very difficult

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to accomplish the differential flotation of a copper activated Cu/Zn ore by means of the conventional flotation process using such depressants as hydroxyl ion, sodium cyanide, or sulphurous acid.

Accordingly, it seems relevant to examine methods for preventing copper activation on sphalerite by eliminating copper ions from the flotation pulp. The precipitation method using hydrogen sulphide or sodium sulphide is one common method for the elimination of copper ions. When sphalerite and sodium sulphide coexist in an aqueous solution containing copper ions, it is not known which reaction occurs first, the formation reaction of copper sulphide by sodium sulphide or the copper activation reaction of sphalerite. Also, in the case where sodium cyanide or sulphurous acid is used as the depressant for sphalerite, it had not been known whether the precipitation method of copper ions by using sodium sulphide could be applied or not.

In this paper, the author studied the applicability of the precipitation method of copper ions by using sodium sulphide.

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 out 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 to eliminate fine particles. These samples were used for the experiment after being kept in a vacuum desicator.

A qualitative analysis of the mineral sample was done with a JACO spectrograph. From the results of the spectroscopic analysis of the mineral samples, it was confirmed that each of the mineral samples was pure enough for the purpose of this study.

3. Prevention of Copper Activation on Sphalerite by Sodium Sulphide

3.1. Measurement of Adsorption Amounts of Copper Ions on Sphalerite

First, the amounts of copper ions adsorbed on sphalerite in the case of the prevention of copper activation by sodium sulphide were measured. The preparation of the used sample was as follows: the 65~100 mesh fraction of sphalerite 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 a vacuum desicator.

The experimental procedure was as follows: one gram of —200 mesh sphalerite sample was immersed in a solution of known pH value, and then added simultaneously to copper sulphate of a known concentration and sodium sulphide of various concentrations to the above solution. After the total volume of the solution was diluted to 50 ml, the solution stood for one hour at room temperature. The initial concentration of copper ions in this experiment was 1×10^{-4} mole/1. The adjustment of pH was made with Britton and Robinson's buffer solution.

The supernatant of the mixture solution was removed by the decantation method, and the sample was then washed thoroughly by distilled water. After the sample obtained in this way was dissolved by a nitric acid solution (1 : 1), the adsorption amounts of copper ions on sphalerite were measured by the Jarrel Ash atomic adsorption spectrometer. The results obtained are shown in Fig. 1. The adsorption amounts of copper ions on sphalerite in Fig. 1 are shown as 100% of the adsorption amounts in the case where sodium sulphide is not added to the pulp.

The specific surface area of the —200 mesh sphalerite was found to be 1137 cm^2/g, as measured by the BET method with nitrogen gas. Considering the effective occupied area of copper ions on sphalerite to be 20.8 $Å^2$,[1] the coverage per cent theoretically calculated from the adsorption amounts of copper ions and specific surface was about 300%, i.e., three molecular layers.

As shown in Fig. 1, it is recognized that the adsorption amounts of copper ions on

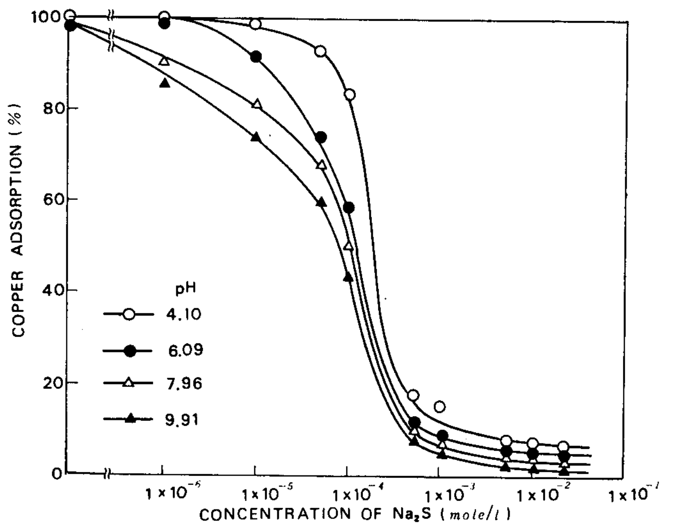

Fig. 1. Relationship between the copper adsorption on sphalerite and the concentration of sodium sulphide.

sphalerite decrease remarkably in the case where sodium sulphide concentration is more than 1×10^{-4} mole/l under a known concentration of copper sulphate ($=1 \times 10^{-4}$ mole/l). When the sodium sulphide concentration is 1×10^{-3} mole/l over pH 6, the data indicates that the adsorption amounts of copper ions are less than 5%. Under this condition, it is recognized that the adsorption amounts of copper ions on sphalerite are completely prevented by adding sodium sulphide.

3.2. Flotation Tests

Next, a series of flotation tests of sphalerite in the case of the prevention of copper ions by sodium sulphide was carried out. The floatability of sphalerite was measured by a Hallimond tube. Compressed nitrogen gas was used for the gas bubble production.

It may be considered that the various gases adsorbed on the mineral surface hinder the floatability of sphalerite. Therefore, after the gases adsorbed on the mineral surface were removed by a vacuum pump, the flotation tests were carried out.

In a series of tests, one gram of 65~100 mesh sphalerite was weighed and then sphalerite was prepared by the pretreatment as mentioned above. One gram of sphalerite was slowly agitated in a solution of 50 ml containing known amounts of copper sulphate and various amounts of sodium sulphide. The solution was kept at a temperature of 25°C for one hour. The supernatant of the mixture solution was removed by the decantation method, and then the sample was washed thoroughly by distilled water. The sample obtained in this way was conditioned for three minutes in a solution of about 150 ml having various pH values. The flotation time was six minutes. The float and

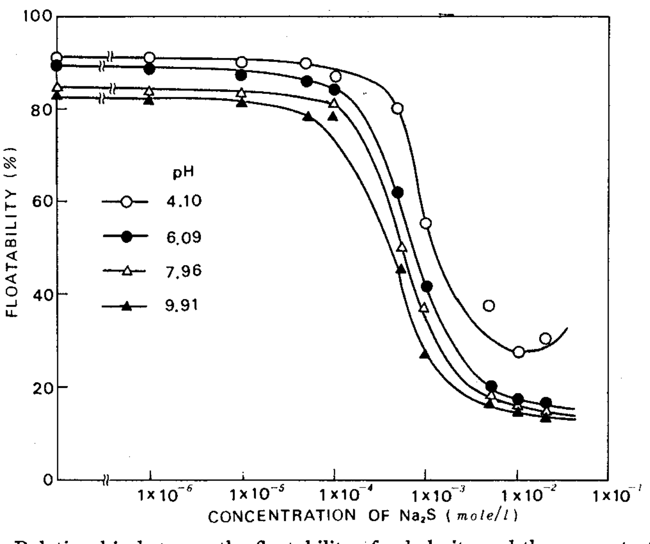

Fig. 2. Relationship between the floatability of sphalerite and the concentration of sodium sulphide in the case where copper ions exist in the flotation pulp.

sink were dried and weighed. The flotation conditions were as follows: potassium ethyl xanthate, 25 mg/l; pH, 10.5.

Fig. 2 shows the results obtained with sphalerite. In this experiment, it has been confirmed from preliminary flotation tests that the floatability of unactivated sphalerite is about 11%. When the concentration of sodium sulphide added was less than the equivalent amounts for the copper sulphate concentration of 1×10^{-4} mole/l, sphalerite floated considerably in a wide range of pH values. When the concentration of sodium sulphide added was more than the equivalent amounts for the copper sulphate concentration of 1×10^{-4} mole/l, the floatability of sphalerite was sharply lowered. When the concentration of sodium sulphide was more than 7×10^{-4} mole/l for the copper sulphate concentration of 1×10^{-4} mole/l, the floatability of sphalerite was about 14%. In these conditions, it was confirmed that the adsorption of copper ions on sphalerite was completely prevented.

According to the same method as C.H.G. Bushell and collaborators[2] calculated thermodynamically, about the consideration of copper activation on pyrite, it was not known whether the formation reaction of copper sulphide by sodium sulphide and the reaction of copper activation on sphalerite occur selectively or not. From the above results, however, it was confirmed that the effect of sodium sulphide on the prevention of copper activated sphalerite was remarkable.

4. Influence of Sodium Cyanide as Depressant on Effect of Sodium Sulphide in Prevention of Copper Activation

The differential flotation with sodium cyanide was often carried out after precipitating copper ions in the flotation pulp by sodium sulphide. When sodium cyanide was present in the flotation pulp, however, copper sulphide formed with the addition of sodium sulphide redissolved by the addition of sodium cyanide. Therefore, it is suspected that the effect of sodium sulphide on the prevention of copper activation for sphalerite is lost by sodium cyanide.

Forming cyanogen (C_2N_2) in the case where both sodium cyanide and copper ions are present in the solution, cupric ions are reduced to cuprous ions. On the other hand, it is known that the complex ions or complexes of copper cyanide are formed by reacting cupric ions and cuprous ions with cyanide ions.

These reactions are complicated by the formation of the complex ions of zinc cyanide produced simultaneously. Accordingly, the theoretical analysis of the system containing sodium sulphide, copper sulphate and sodium cyanide in the solution is very difficult and complicated. To confirm the effect of sodium sulphide, the author experimented by flotation tests with a Hallimond tube when sodium cyanide was contained in the flotation pulp.

In the first place, a series of flotation tests was carried out on the depressing effect of sphalerite with sodium cyanide. The flotation conditions were as follows: 65~100 mesh sphaleiite, 1 g; potassium amyl xanthate, 30 mg/l; flotation time, 6 minutes.

Fig. 3 shows the results of the flotation tests on taking the pH values as the parameter and varying the concentration of sodium cyanide. As shown in Fig. 3, the the floatability shows more than 50% in the addition of sodium cyanide 1,000 mg/l at pH 7.00 when potassium amyl xanthate is used as the collector. With the increase of the alkalinity in the flotation pulp, it is confirmed that the depressing effect of sodium cyanide on sphalerite is remarkable, that is, sphalerite is depressed with the addition of sodium cyanide 300 mg/l at pH 8.30. The dotted chain line in Fig. 3 shows the floatability at pH 9.10 on sphalerite activated with 6×10^{-4} mole/l of copper sulphate. The copper activated sphalerite leads to a flotation of more than 80% with the addition of sodium cyanide in excess of 1,000 mg/l.

In the case where sodium cyanide was used as the depressant, the effect of sodium sulphide on the prevention of copper activation was examined from the flotation tests by using a Hallimond tube. The experimental procedure was as follows: copper sulphate and sodium sulphide were added simultaneously to the suspension containing one gram of 65~100 mesh sphalerite, then sodium cyanide was added, and the pH value of the suspension was regulated. The initial concentration of copper sulphate and sodium sulphide was maintained constant at 6×10^{-4} mole/l in a series of tests. The sodium cyanide concentration was varied between zero and 200 mg/l to examine the effect of sodium sulphate on the prevention of copper activation.

Fig. 4 shows the results obtained. Up to a certain addition of sodium cyanide, the floatability of sphalerite increases with the increase of sodium cyanide in all pH ranges. By increasing the concentration of sodium sulphide to over 30 mg/l, however, the depressing effect of sodium cyanide on sphalerite becomes distinguished by the addition of sodium sulphide.

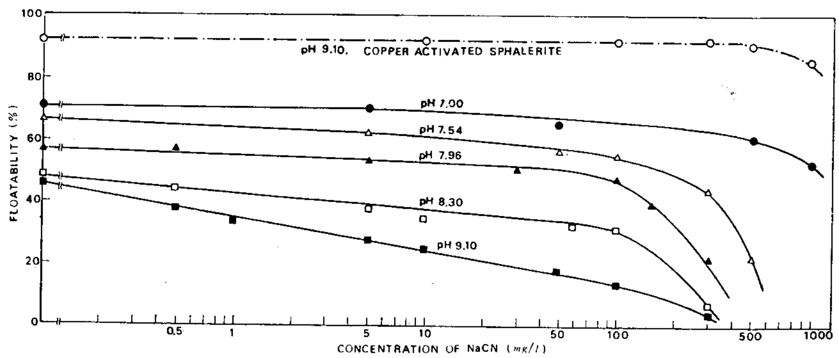

Fig. 3. Relationship between the floatability of sphalerite and the concentration of sodium cyanide.

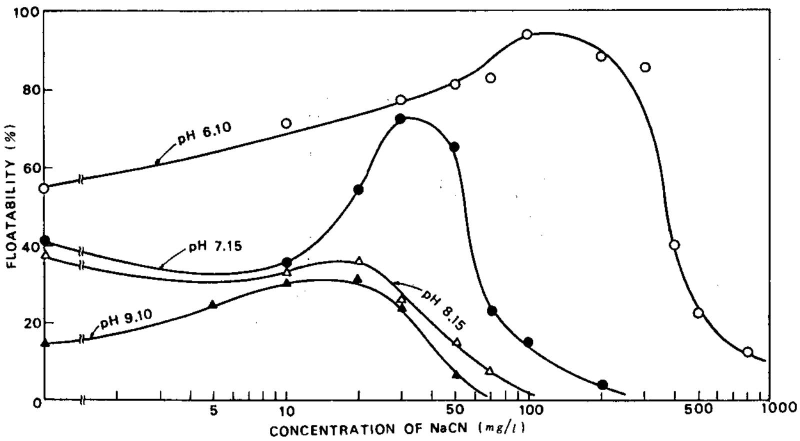

Fig. 4. Effect of sodium cyanide on the floatability of sphalerite when copper activation of sphalerite is prevented by sodium sulphide.

In the contrast with Fig. 3, it is recognized that the depression of sphalerite is remarkable with the addition of sodium sulphide. This occurs only with the addition of sodium cyanide to increase the floatability of sphalerite up to a certain addition of sodium cyanide. The author hypothesized that this phenomenon was caused by coating copper sulphide particles or copper cyanide complexes precipitated by sodium sulphide on the sphalerite surface. The analysis of this phenomenon was examined by the following experiment.

The author adopted the procedure which D. W. Fuerstenau and his collaborators[3] had determined for the adsorption density of iron oxide slime on quartz. At first, given amounts of solutions of 6×10^{-4} mole/l of sodium sulphide and copper sulphate were added at the same time. Then, after sodium cyanide was added to the solution containing sodium sulphide and copper sulphate, the pH of the solution was adjusted. One gram of 65~100 mesh sphalerite was taken in the Elenmyer flask, and 50 ml of the above solution added to it. It was stirred slowly for about 30 minutes. The sample of sphalerite was fully purified with the above solution. The copper adsorbed on the surface of sphalerite was leached by using sodium cyanide. The amounts of copper were quantitatively determined by the atomic adsorption spectrometer. Fig. 5 shows the adsorption density of copper on sphalerite at pH 7.15 and 9.10, varying the concentration of sodium cyanide. As shown in Fig. 5, the adsorption density showed a maximum value at 20~30 mg/l of the sodium cyanide concentration in both pH values of 7.15 and 9.10. Over 30 mg/l of sodium cyanide concentration, the adsorption density decreased remarkably. On the other hand, when the sphalerite treated with the above solution was washed with distilled water, the adsorption density of copper on sphalerite was zero. From this result, the adsorption density of copper shown in Fig. 5 could not be thought

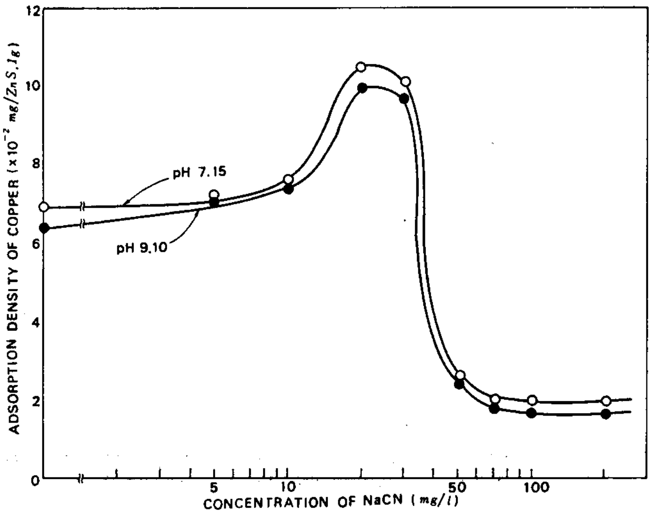

Fig. 5. Effect of sodium cyanide on the copper adsorption density of sphalerite.

to be adsorption by copper ions. Therefore, it was supposed that it was due to the coating of sodium sulphide or copper cyanide complexes precipitated by sodium sulphide. Contrasting Fig. 5 with Fig. 4, it was recognized that both results coincided very well.

Fig. 6 shows the relationship between the adsorption density of copper on sphalerite and the pH value in the same experiment shown in Fig. 5. The concentration of sodium cyanide was constant at 20 mg/l. As shown in Fig. 6, it was recognized that the ad-

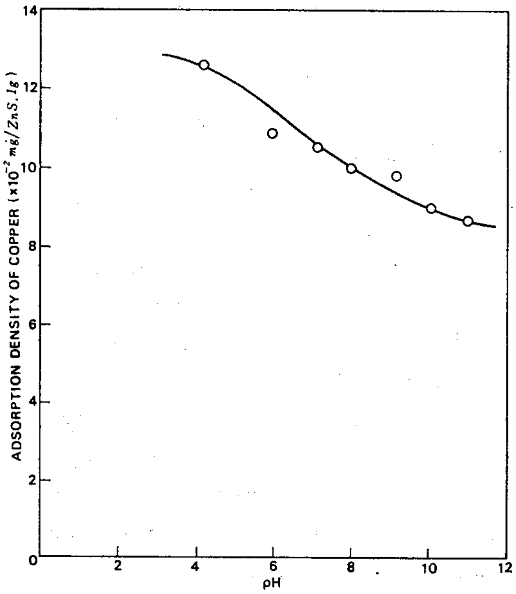

Fig. 6. Effect of pH on the copper adsorption density of sphalerite.

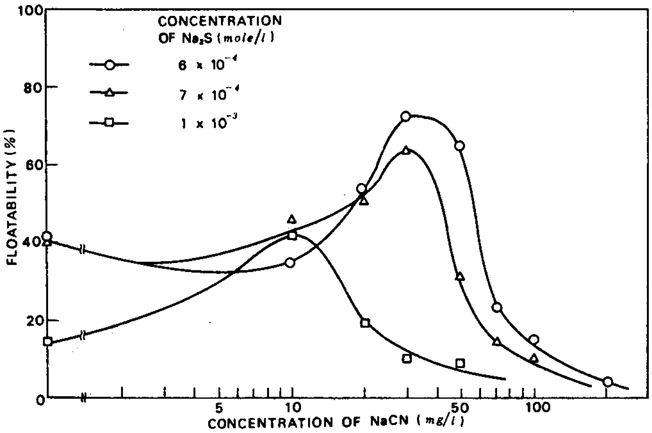

Fig. 7. Effect of sodium cyanide on the floatability of sphalerite in the case where copper ions exist in the flotation pulp.

sorption density decreased with the increase of pH.

Fig. 7 shows the results which measured the floatability, varying the concentration of sodium sulphide under the constant pH value of 7.15. The tendency of the obtained results was similar to that of Fig. 4.

When the concentration of sodium sulphide was 6×10^{-4} mole/l, sphalerite was floated to about 4% of the floatability with the addition of 200 mg/l of sodium cyanide and was almost depressed. It was recognized that sphalerite was depressed at a lower concentration of sodium cyanide with the addition of more sodium sulphide. Therefore, when cyanide ions are present in the flotation pulp, the relationship between the amounts of copper ions and sodium sulphide contained in the solution is important.

5. Effect of Sodium Sulphide on Prevention of Copper Activation by Sulphurous Acid as Depressant

Sulphurous acid (SO_2 gas) has been extensively used as a depressant for the differential flotation of complex sulphide ores. Therefore, it is useful to examine the effect of sodium sulphide on the prevention of copper activation in the case where sulphurous acid is used as a depressant.

After adding copper sulphate and sodium sulphide at the same time to the suspension containing one gram of 65~100 mesh sphalerite, sulphurous acid was added. Then the pH value of the suspension was adjusted, and the floatability was measured by a Hallimond tube.

In these experiments, the initial concentrations of copper sulphate and sodium sulphide were 6×10^{-4} mole/l. The concentration of added sulphurous acid was varied from zero to 100 mg/l. The concentration of sulphurous acid was quantitatively

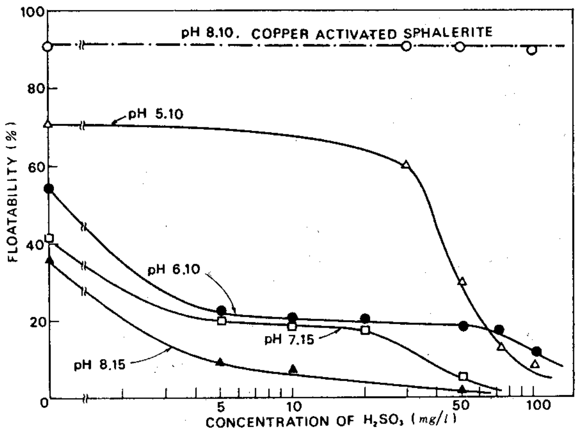

Fig. 8. Effect of sulphurous acid on the floatability of sphalerite when copper activation of sphalerite is prevented by sodium sulphide.

determined by Iodometry. The results obtained are shown in Fig. 8. As shown in Fig. 8, the effect of depression on sphalerite by sulphurous acid is remarkable with the increase of the pH, and sphalerite is almost completely depressed by the addition of 50 mg/l of sulphurous acid at pHs of 7.15 and 8.15. The copper activated sphalerite with a copper sulphate concentration of 6×10^{-4} mole/l could not be depressed by adding 100 mg/l of sulphurous acid at pH 8.10, and the floatability of sphalerite was more than 90%. When an excess of sodium sulphide coexisted with sulphurous acid, we often encountered the phenomenon that the colloidal sulphur particles formed by the addition of sulphurous acid in the region of acidity were adsorbed on the surface of sulphide minerals, and that the depression of sulphide minerals become very difficult. This phenomenon was perhaps caused by the decomposition of the polysulphides being contained in the sodium sulphide. This was especially notable in the acidic region. When sodium sulphide is used, therefore, acidifying the flotation pulp should be avoided.

From the above results, though sulphurous acid is used as a depressant, it is recognized that the effect of sodium sulphide on the prevention of copper activation of sphalerite is remarkable.

6. Effect of Sodium Sulphide on Prevention of Copper Activation in Cu/Zn Differential Flotiton

In sections 4 and 5, the prevention of copper activation of sphalerite in the case where sodium cyanide and sulphurous acid existed in the flotation pulp was examined from the flotation tests by a Hallimond tube. As the influence of sodium sulphide on the floatability of sulphide minerals is considerable, it is necessary to examine the effect of coexisting sulphide minerals for the flotation on the prevention of the copper activation. Consequently, differential flotation tests were carried out to confirm the effect of sodium sulphide.

6.1. Differential Flotation Tests of Unactivated and Activated Cu/Zn Ores with Copper Ions

Five grams of 65~100 mesh sphalerite and chalcopyrite were weighed respectively, and the flotation tests were carried out by using a 250 ml MS type flotation test machine. After the copper activated mineral samples were treated for one hour with 100 ml of copper ion solution of 6×10^{-4} mole/l, the supernatant was removed by the decantation method, and then the mineral samples were washed thoroughly with distilled water. The samples obtained in this way were conditioned for two minutes in a 225 ml solution for a given pH value. The flotation tests were carried out by varying the pH value. After the given amounts of potassium amyl xanthate and pine oil were added to the pulp, the pulp was agitated for one minute. The flotation time was five minutes. The float and sink were dried and weighed. After the analysis of both products was carried out, the recovery was calculated. The flotation conditions are as follows: potassium amyl xanthate, 30 mg/l; pine oil, 40 mg/l; pulp density, 4% solids.

The results obtained are shown in Fig. 9. Fig. 9 shows the copper and zinc recoveries of the float product in the case where the pH value of the flotation pulp is varied. As shown in Fig. 9, it is recognized that the depression of the copper unactivated sphalerite by only OH^- ion is very difficult, and that the separation of Cu/Zn ores is possible in a strong alkaline solution of over pH 12. The copper activated sphalerite, however, shows the same floatability as chalcopyrite, so the separation of the

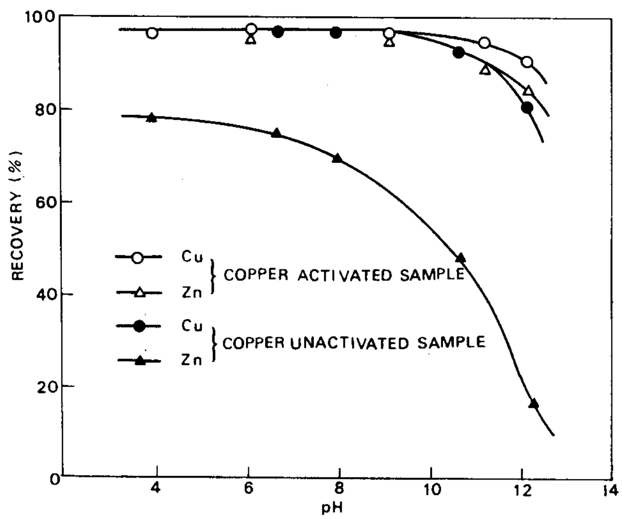

Fig. 9. Effect of pH on chalcopyrite and sphalerite recoveries in the separation of Cu/Zn ores.

copper activated Cu/Zn ores is almost impossible.

6.2. Effect of Sodium Sulphide on Prevention of Copper Activation in Cu/Zn Ores Separation under the Existence of Sodium Cyanide in a Flotation Pulp

The differential flotation tests of Cu/Zn ores were carried out by the same experimental procedure as in section 4. The results obtained are shown in Fig. 10 and Fig. 11.

Fig. 10 shows the copper and zinc recoveries of the float product in the case where the differential flotation tests of Cu/Zn ores are carried out by varying the added amounts of sodium cyanide at pH 8.15 and 9.00 of the flotation pulp. As shown in Fig. 10, the depression of sphalerite at pH 8.15 of the pulp is remarkable with the increase of the added amounts of sodium cyanide. It is recognized that sphalerite is completely depressed in over 100 mg/l of the added sodium cyanide. In this condition, the recovery of sphalerite is less than 10%. However, the recovery of chalcopyrite decreases remarkably when over 100 mg/l of sodium cyanide is added. Accordingly, it is necessary to pay careful attention when sodium cyanide is used for the prevention of the copper activation by sodium sulphide in the differential flotation of Cu/Zn ores. At pH 9 of the flotation pulp, it is recognized that the recovery of chalcopyrite in the float product decreases remarkably when the addition of sodium cyanide is over 70 mg/l.

Under the conditions of this experiment, the optimum conditions obtained from this experiment are as follows: at pH 8.15, the addition of about 100 mg/l of sodium cyanide; at pH 9.00, 30~50 mg/l. Under these experimental conditions, it is recognized that the separation of Cu/Zn ores is most satisfactory and that the copper activation is prevented by using sodium sulphide.

Sodium sulphide acts as a depressant for such sulphide minerals as chalcopyrite and

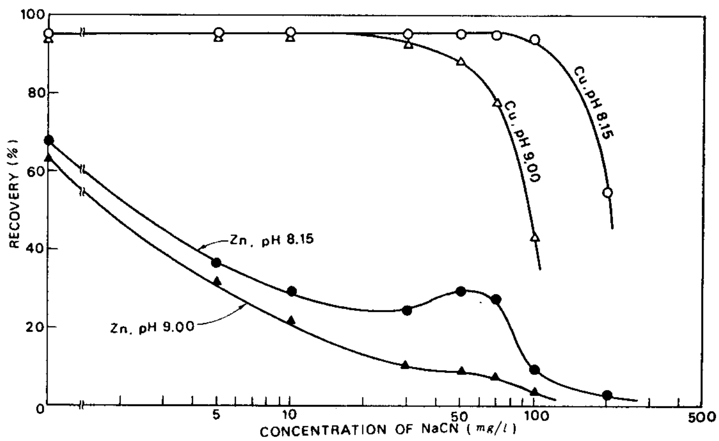

Fig. 10. Effect of sodium cyanide on chalcopyrite and sphalerite recoveries in the separation of Cu/Zn ores.

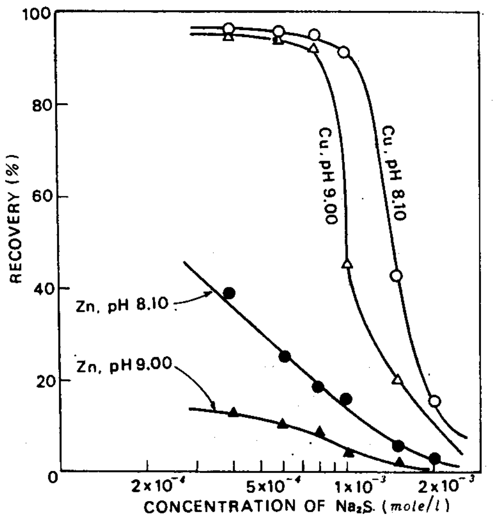

Fig. 11. Effect of sodium sulphide on chalcopyrite and sphalerite recoveries in the separation of Cu/Zn ores when sodium cyanide exists in the flotation pulp.

galena, etc. Therefore, when sodium sulphide is used for the prevention of copper activation, it is necessary to use sodium sulphide within a range which does not depress the floatability of sulphide minerals. Fig. 11 shows the copper and zinc recoveries of the float product in the case where the differential flotation tests of Cu/Zn ores were carried out, varying the additions of sodium sulphide. The concentration of sodium cyanide in the flotation pulp is constant, that is, 30 mg/l. As shown in Fig. 11, when the concentration of sodium sulphide is more than the added concentiation of copper sulphate at both pH 8.10 and 9.00 of the flotation pulp, that is, more than 1×10^{-3} mole/l and 8×10^{-4} mole/l respectively, the residual concentration of sodium sulphide in the flotation pulp increases. In these conditions, the depression of chalcopyrite by sodium sulphide is recognized and the copper recovery tends to be decreased. However, when the concentration of sodium sulphide in the flotation pulp is more than 2×10^{-3} mole/l, chalcopyrite is depressed considerably by sodium sulphide, and under such conditions as mentioned above. The separation of Cu/Zn ores under these conditions tends to be difficult.

From the above results, it was confirmed that the separation of Cu/Zn ores was successful by adding the optimum concentration of sodium sulphide even if copper ions existed in the flotation pulp.

6.3. Effect of Sodium Sulphide on the Prevention of Copper Activation in Cu/Zn Ores Separation under the Existence of Sulphurous Acid in a Flotation Pulp

After copper sulphate and sodium sulphide were simultaneously added to the suspension containing five grams of 65~100 mesh sphalerite and chalcopyrite respectively, sulphurous acid was added to the suspension and the pH value of the pulp was regulated. The flotation tests of Cu/Zn ores separation were carried out by using a 250 ml MS type flotation machine. The results obtained are shown in Figs. 12, 13 and 14.

Fig. 12 shows the results obtained by varying the concentration of sulphurous acid, that is, 0~500 mg/l. The initial concentration of copper sulphate and sodium sulphide is 6×10^{-4} mole/l, and the pH value of the pulp is constant, at pH 7.10. As shown in Fig. 12, the sphalerite recovery of the float product decreases remarkably with the increase of the added concentration of sulphurous acid. On the other hand, sphalerite is nearly depressed over 100 mg/l of the concentration of sulphurous acid when the pH value of the flotation pulp is 7.10. In these conditions, the depressing effect of sulphurous acid on chalcopyrite is not recognized. Accordingly, it is recognized that separation of Cu/Zn ores is successful over 100 mg/l of the concentration of sulphurous acid.

Fig. 13 shows the results obtained by varying the pH value of the flotation pulp. The initial concentration of copper sulphate and sodium sulphide is 6×10^{-4} mole/l and the added concentration of sulphurous acid is constant, 100 mg/l. As shown in Fig. 13, the separation of Cu/Zn ores in an acidic solution of less than pH 7.00 is impossible because the sphalerite floats. In the case of an alkaline flotation pulp of over pH 7.00, however, the separation of Cu/Zn ores is successful because sphalerite is completely depressed by sulphurous acid. In these conditions, it is recognized that the effect of the prevention of copper ions by sodium sulphide is remarkable.

Fig. 14 shows the results obtained by varying the added concentration of sodium sulphide at pH 5.00, 6.50 and 8.10. The added concentration of copper sulphate and

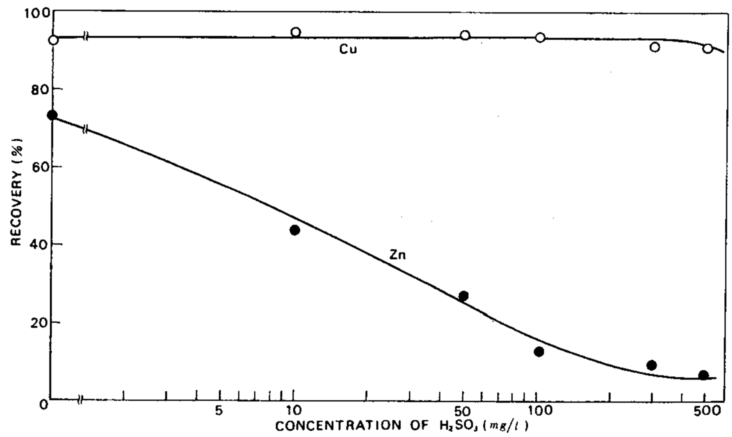

Fig. 12. Effect of sulphurous acid on chalcopyrite and sphalerite recoveries in the separation of Cu/Zn ores.

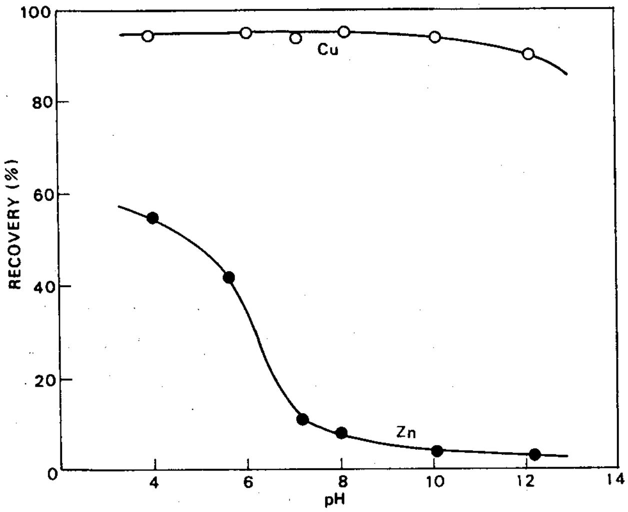

Fig. 13. Effect of pH on chalcopyrite and sphalerite recoveries in the separation of Cu/Zn ores when sulphurous acid exists in the flotation pulp.

sulphurous acid is 6×10^{-4} mole/l and 100 mg/l, respectively. As shown in Fig. 14, the effect of the prevention of copper activation by sodium sulphide is not recognized at pH 5.00, because sphalerite is similar to chalcopyrite despite increasing the amount of sodium sulphide. Consequently, the separation of Cu/Zn ores is impossible in the above conditions. At pH 6.50 and 8.10, the depression of sphalerite is considerable with the increase of the added concentration of sodium sulphide, but the depressing

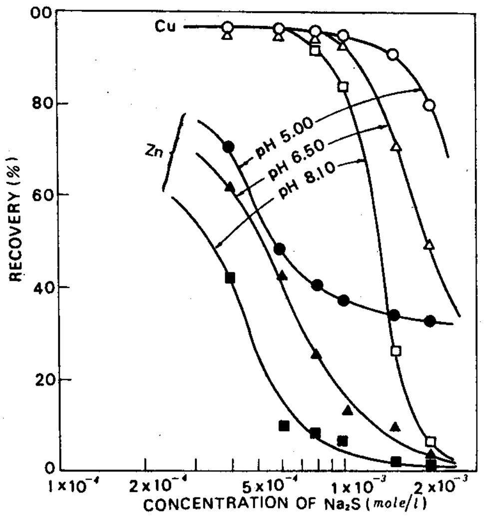

Fig. 14. Effect of sodium sulphide on chalcopyrite and sphalerite recoveries in the separation of Cu/Zn ores when sulphurous acid exists in the flotation pulp.

effect of sodium sulphide for chalcopyrite is shown over 1×10^{-3} mole/l of sodium sulphide, and the copper recovery decreases. As is clearly shown in Fig. 14, however, the separation of Cu/Zn ores is not successful at pH 6.50. When sulphurous acid is used as the depressant, it is recognized that the separation of Cu/Zn ores is successful in an alkaline solution over pH 8.10.

7. Conclusions

In order to overcome the difficulties of the Cu/Zn differential flotation resulting from copper ions, the effect of sodium sulphide on the prevention of copper activation for sphalerite was studied. Further, it was examined whether the prevention of copper activation for sphalerite by sodium sulphide was possible or not, when sodium cyanide or sulphurous acid was used as a depressant.

The results of this study are summarized as follows:

1) It was recognized from the adsorption measurement of copper ions on sphalerite that the adsorption amounts of copper ions on sphalerite increased remarkably in the case where the concentration of sodium sulphide was more than the concentration of copper ions existing in the flotation pulp, and that copper adsorption on sphalerite was completely prevented by sodium sulphide over pH 6.

2) From the flotation tests of sphalerite, it was recognized that the effect of prevention of copper activation by sodium sulphide was remarkable, because the floatability of sphalerite decreased considerably with the addition of larger amounts than the concentration of copper ions existing in the flotation pulp, and coincided nearly with the floatability of the unactivated sphalerite.

3) From the results examined on the effect of the prevention of copper activation by sodium sulphide in the case where sodium cyanide was used as a depressant, it was recognized that the floatability of sphalerite increased by a certain addition of sodium cyanide. It was confirmed that this phenomenon was caused by the coating of copper sulphide particles or by a copper complex precipitated by sodium sulphide on the sphalerite surface. Increasing the concentration of sodium cyanide over pH 8, however, it was recognized that the floatability of sphalerite was completely depressed by the addition of 50～100 mg/l of sodium sulphide, and that the depressing effect of sodium cyanide was remarkable with respect to the non-addition of sodium sulphide.

4) From the results examined on the effect of copper activation by sodium sulphide in the case where sulphurous acid exists in the flotation pulp, the depressing effect of sphalerite by sulphurous acid was not recognized because the colloidal sulphur particles were formed by the decomposition of polysulphides contained in the sodium sulphide. However, it was recognized that sodium sulphide showed a depressing effect for sphalerite by the addition of larger amounts than the added concentration of copper ions at

over pH 6.10. By the above conditions, it was confirmed that the effect of prevention of copper activation by sodium sulphide was remarkable.

5) In the separation of Cu/Zn ores, it is necessary that the sodium sulphide for the prevention of copper activation does not influence the floatability of chalcopyrite. From the results obtained, adding sodium sulphide of 1×10^{-3} mole/l at pH 8.10 and over 8×10^{-4} mole/l at pH 9.00 against the copper ion concentration of 6×10^{-4} mole/l when sodium cyanide was used as a depressant, it was recognized that the floatability of chalcopyrite decreased remarkably. It was confirmed that the optimum concentration of sodium sulphide was $6\times10^{-4}\sim8\times10^{-4}$ mole/l against the copper ion concentration of 6×10^{-4} mole/l.

6) It was recognized that excess sodium sulphide influenced adversely the floatability of chalcopyrite, and also when sulphurous acid was used as a depressant. It was confirmed that the optimum concentration of sodium sulphide was $6\times10^{-4}\sim1\times10^{-3}$ mole/l at pH 8.10 against the copper ion concentration of 6×10^{-4} mole/l, and that the floatability of chalcopyrite decreased remarkably over 1×10^{-3} mole/l of the sodium sulphide concentration.

From the results obtained in this study, it was recognized that the effect of the prevention of copper activation by sodium sulphide was remarkable, and that also in the case where sodium cyanide or sulphurous acid was used as a depressant, the separation of Cu/Zn ores was successful by adding the optimum concentration of sodium sulphide.

References

1) A. M. Gaudin, D. W. Fuerstenau and G. W. Mao: Trans. AIME, Vol. 214, 1959, p. 430.
2) C. H. G. Bushell and C. J. Krauss: Can. Min. Bull., Vol. 55, No. 601, 1962, p. 314.
3) D. W. Fuerstenau, A. M. Gaudin and H. L. Miaw: Min. Eng., July 1958, p. 792.