

Applicability of Precipitation-Flotation Method for Differential Separation of Cadmium from Zinc in Synthesized Waste Cyanide Water

By

Hiroshi MATSUBARA*, Yoshitaka NAKAHIRO**,
Kensaku MURAKAWA*** and Takahide WAKAMATSU**

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Abstract

The removal of heavy metal from synthesized waste cyanide water is achievable by a precipitation-flotation method. However, the differential separation of constituting metals by this method has been thought to be very difficult.

The authors found that the addition of some decomposing reagents to the synthesized waste cyanide water of cadmium and zinc can improve the separation characteristics of these metals. The present study deals with the applicability of the precipitation-flotation method for the differential separation of cadmium from zinc in synthesized waste cyanide water. The proposed method was to use sodium sulphide as a decomposing reagent in the first stage of flotation and hydrogen peroxide in the second stage in order to decompose the Cd-CN and Zn-CN complexes, respectively. Furthermore, the use of such a cation flocculant as FC-80 was considerably effective for the removal of the Cd-CN complex.

Based on a series of fundamental flotation tests, actual differential flotation tests were made. The separation of cadmium from zinc in synthesized waste cyanide water was found to be satisfactory.

This method can be effective for the differential separation of difficult-to-separate colloidal precipitates from liquids by the sedimentation method.

1. Introduction

The general practice in the differential flotation of Pb/Zn ores is to float a lead concentrate, depressing the zinc minerals. After the lead flotation, the zinc minerals are copper-activated and floated selectively. Depression of the zinc minerals in the lead flotation circuit is usually achieved by the use of cyanide, frequently in the presence of zinc sulphate. In many flotation plants of Pb/Zn ores, cyanide ions are contained in waste water besides such heavy metal ions as cadmium and zinc. Ge-

* National Research Institute for Pollution and Resources, Ministry of Industrial Trade and Industry.

** Department of Mineral Science and Technology.

*** Sumitomo Metal Industries Ltd.

nerally, heavy metal ions form complexes with cyanide as well as with others complexing agents. For this reason, the treatment of waste water solutions disposed from a flotation plant of Pb/Zn ores possesses many difficulties.

The authors found that a precipitation-flotation method was successfully applicable to the removal of chromium compound¹⁾, Cd-CN²⁾, Cu-CN³⁾ and Zn-CN complexes⁴⁾ from synthesized waste cyanide water. After that, the separation of cadmium from copper in synthesized waste cyanide water by a precipitation-flotation method was discussed and was found to be satisfactory⁵⁾. If the applicability of this method to the separation of other metals is promising, the sludges, which contain such harmful heavy metal ions as cadmium and zinc, are able to be reutilized. As a result, it is possible that the treatment of waste water is carried out by the closed system.

In this study, the applicability of the precipitation-flotation method for the differential separation of cadmium from zinc in synthesized waste cyanide water was discussed.

2. Experimental Procedure

Pure metal cadmium and zinc (99.99% plus each) were dissolved with nitric acid, and then diluted with distilled water to the desired concentrations. A predetermined amount of sodium cyanide was added to the solution of cadmium and zinc ions containing 10 mg/l, respectively. An addition of cyanide ion concentration was 5 mg/l. Sodium sulphide and hydrogen peroxide were used in order to decompose such metal complexes as Cd-CN and Zn-CN. An aqueous solution of ferrous sulphate containing 50 mg/l Fe(II) was used as a precipitant in some cases. Some flocculants were also used because the products of the metal complexes decomposed by adding the decomposing reagents were very fine colloidal precipitates. Two kinds of flocculants were used in this study. One of them was Alkox, and the other was FC-80.

The main constituent of Alkox is polyethylene oxide. The molecular of polyethylene oxide is a polymer which is connected with the ethylene oxide molecular (CH₂CH₂O). The general molecular formula of polyethylene oxide is denoted by HO-(CH₂CH₂O)_n-CH₂CH₂OH, and is soluble in water. The average molecular weight of polyethylene oxide used in this study is six million. Polyethylene oxide is a non-ionic flocculant and the effect of salting out is mild in comparison with other polymer flocculants.

FC-80 is a co-polymer containing acrylamide (CH₂=CHCONH₂) and dimethylaminoethylmetaacrylate ((CH₃)₂NCH₂=C(CH₃)COOHM¹, where M¹ denotes monocation) and is an organic cationic flocculant.

In a series of flotation tests, either potassium ethyl xanthate or sodium oleate was used as a collector while pine oil was used as a frother. The adjustment of pH was made either with sulphuric acid or sodium hydroxide. All chemicals mentioned above were of reagent grade.

Prior to the precipitation-flotation tests, the effect of sodium sulphide on the decomposition of such metal complexes as Cd-CN and Zn-CN were examined. In another test using sodium sulphide, such a collector as potassium ethyl xanthate or sodium oleate was used together with sodium sulphide in order to improve the effect on the precipitation of cadmium and zinc. In a series of precipitation tests with sodium sulphide, sodium sulphide was added to the test solutions containing Cd-CN and Zn-CN complexes for the purpose of decomposition and precipitation. After sodium sulphide was added to the test solutions adjusted to pH 2.20, pH was readjusted to the desired value*. The precipitate was centrifuged at 15,000 rpm ("g" value of about 100) for 15 minutes to remove the colloidal precipitates from the solution. Then the concentrations of cadmium and zinc ions in supernatant liquid were determined by an atomic absorption spectrophotometer. The amounts of cadmium and zinc removed as precipitates were calculated from the difference in the concentration of the solution before and after the precipitation. The analysis of the total cyanide concentration in the supernatant liquid was done by means of the total cyanide distillation method according to the Japanese Industrial Standard⁹⁾. Aliquot of solution was acidified with phosphoric acid, and then ethylenediaminetetraacetic acid was added to the solution. The solution was subjected to distillation to decompose the metal cyanide complexes. The cyanide ions released were collected in distilled solution. The concentration of cyanide ion in the solution was determined electrochemically by a cyanide electrode.

The effect of hydrogen peroxide on the precipitation of the zinc compound was examined for a test solution containing zinc cyanide complexes. A predetermined amount of hydrogen peroxide was added to the test solution of pH 10.5. The solution was kept at ambient room temperature for 20 minutes, followed by the addition of ferrous sulphate to reach a value of 50 mg/l. Then the pH of the solution was accurately adjusted to the desired value. The precipitation test procedure for zinc cyanide solution was the same as in the case of the above mentioned.

A series of precipitation-flotation tests with the addition of sodium sulphide was made with and without ferrous sulphate in the following manner. In the case of using ferrous sulphate as a precipitant, a predetermined amount of the ferrous sulphate solution was added to the test solution to reach a value of 50 mg/l Fe(II) to precipitate the metal compound after treatment for the decomposition of cadmium

* The pH values at those experimental stages will be reported in the figures.

and zinc complexes by sodium sulphide. After the completion of precipitation, a desired amount of sodium oleate or potassium ethyl xanthate as a collector was added to the test solution, followed by the pH adjustment. The flotation was carried out for 5 minutes with the addition of 13 mg/l pine oil as a frother using a 2,000 ml capacity laboratory flotation machine of the modified Fagergren type. This laboratory flotation machine has specially designed guide vanes around the impeller which facilitates creating a favourable flow pattern in the cell and drawing much more air into the cell than the conventional ones. When a chemical precipitate is floated in the flotation cell, a violent flow or strong agitation disperses the precipitate finely and acts adversely on the precipitate flotation. Accordingly, the present authors are expecting the appearance of a flotation cell suitable for chemical precipitate. The authors think that the laboratory cell used is one of the cells suitable for chemical precipitate as well as for fine ore particles.

In the case of using such flocculants as Alkox and FC-80, a predetermined amount of the flocculant was added to the test solution after treatment for the decomposition of cadmium and zinc complexes by sodium sulphide. After the completion of coagulation with FC-80, the flotation tests were carried out in the same manner as mentioned above. In this case, sodium oleate of 25 mg/l was added as a collector.

The flotation tests in the case of using hydrogen peroxide were carried out in the following manner. After treatment for the decomposition of metal cyanide complexes by hydrogen peroxide, a predetermined amount of ferrous sulphate solution was added to the test solution to reach a value of 50 mg/l Fe(II) precipitate the metal compound. After the completion of precipitation, sodium oleate of 25 mg/l was added to the test solution as a collector, followed by flotation. The flotation test procedure was the same as the above mentioned.

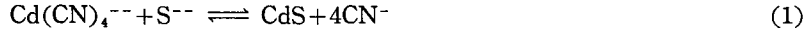
The differential flotation of cadmium from zinc in synthesized waste cyanide water was done according to the flowsheets shown in Figs. 14 and 15. As can be seen in these figures, the differential flotation tests were carried out with and without the treatment of coagulation by FC-80.

3. Experimental Results and Discussion

3.1. Effect of Sodium Sulphide on Separation of Cadmium from Zinc in Synthesized Waste Cyanide Water by Precipitation-Flotation Method.

It has been found that the removal of heavy metal cyanide complexes in waste water by the sedimentation method with iron hydroxide or the precipitation flotation method is very difficult with the increase of concentrations of cyanide ions. The authors had observed that sodium sulphide was effective for the removal of Cd-CN

complexes in waste water⁷⁾. The reaction for decomposition of cadmium cyanide complexes with sodium sulphide would be:



The above reaction is known to proceed quantitatively⁸⁾. Compared to the stability of cyano-complexes of cadmium, the stability of cadmium sulphide is far greater, because the solubility product of cadmium sulphide is very low.

Prior to the differential separation of cadmium from zinc in synthesized waste cyanide water by a precipitation-flotation method, the precipitation characteristics of Cd-CN and Zn-CN complexes were examined by precipitation tests with sodium sulphide.

Fig. 1 shows the effect of the pretreatment with the addition of sodium sulphide on the differential precipitation of Cd-CN and Zn-CN complexes. In the acidic region of pH below 4, the cadmium precipitation was about 74%, but the precipitation of zinc by the addition of sodium sulphide was not observed in the region of pH below 4. However, the precipitation of zinc increased with the increase of the pH value. Accordingly, the pH value must be adjusted in order to separate cadmium from zinc in waste cyanide water by the precipitation method.

Fig. 2 shows the effect of the addition of sodium sulphide and sodium oleate on the differential precipitation of Cd-CN and Zn-CN complexes. In this case, the pH value for the precipitation treatment was 4.0. As shown in Fig. 2, the preci-

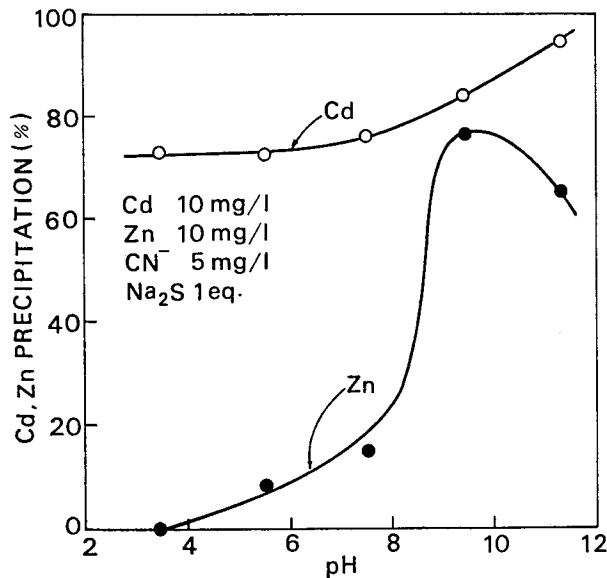


Fig. 1. Effect of the pretreatment by the addition of sodium sulphide on the differential precipitation of Cd-CN and Zn-CN complexes.

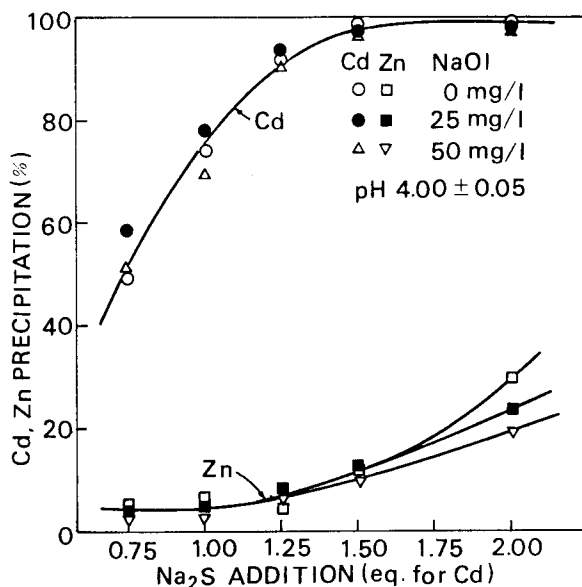


Fig. 2. Effect of the addition of sodium sulphide and sodium oleate on the differential precipitation of Cd-CN and Zn-CN complexes.

precipitation of cadmium and zinc increase with the addition of sodium sulphide. On the other hand, the effect of the addition of sodium oleate for the precipitation of both metals was not observed. From these results, the optimum addition of sodium sulphide on the differential precipitation of Cd-CN and Zn-CN complexes was 1.0 to 2.5 equivalents.

Fig. 3 shows the effect of the addition of sodium sulphide and potassium ethyl xanthate on the differential precipitation of Cd-CN and Zn-CN complexes. As can be seen from Fig. 3, when sodium sulphide is used in common with potassium ethyl xanthate, the effect of sodium sulphide for the precipitation of cadmium is considerable with an increased addition of potassium ethyl xanthate. On the other hand, sodium sulphide for the precipitation of zinc was not effective even if sodium sulphide was used in common with potassium ethyl xanthate.

From the results obtained above, it was found that the differential precipitation of Cd-CN and Zn-CN complexes was possible under the optimum conditions by using sodium sulphide. In the range of pH below 4, cadmium of about 74% was precipitated by adding sodium sulphide 1.00 to 1.25 equivalents, but the Zn-CN complex remained in the solution under these conditions. In the case of adding sodium sulphide together with potassium ethyl xanthate, the effect of sodium sulphide for the precipitation of cadmium was especially effective. In this case, the precipitation of cadmium was over 90% by using both sodium sulphide of 1 equivalent and

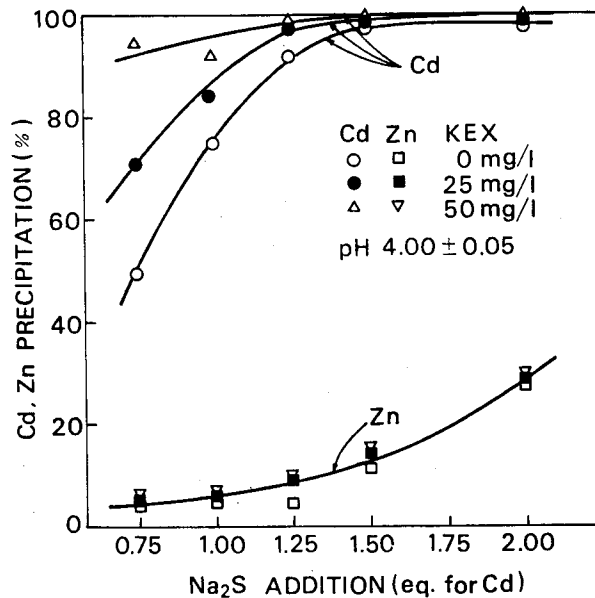


Fig. 3. Effect of the addition of sodium sulphide and potassium ethyl xanthate on the differential precipitation of Cd-CN and Zn-CN complexes.

potassium ethyl xanthate of 50 mg/l, and the precipitation of zinc was only about 5%.

Based on the results obtained above, the effect of sodium sulphide on the separation of cadmium from zinc in synthesized waste cyanide water was examined by the precipitation-flotation method.

Fig. 4 shows the effect of pH on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with both sodium sulphide and ferrous sulphate. In this case, it was observed that the effect of co-precipitation was considerable by adding ferrous salts. Thus, the applicability of the differential separation of Cd-CN from the Zn-CN complex was not found because both metal complexes showed the same flotation behavior all over the pH region.

Then, after the pretreatment of sodium sulphide, the flotation test was carried out by using sodium oleate as a collector without ferrous salts. The results obtained are given in Fig. 5. In the range of pH below 5.5, the removals of Cd and Zn were 94% and 16%, respectively. From the results obtained, it was found that the addition of ferrous salts for the separation of cadmium from zinc in synthesized waste cyanide water was unfavorable in the case of using sodium sulphide.

Fig. 6 shows the effect of the pretreatment with the addition of sodium sulphide on the removal of Cd-CN and Zn-CN complexes by the precipitation-flotation method with sodium oleate. In this experiment, the flotation pH was constant at 4.00. As

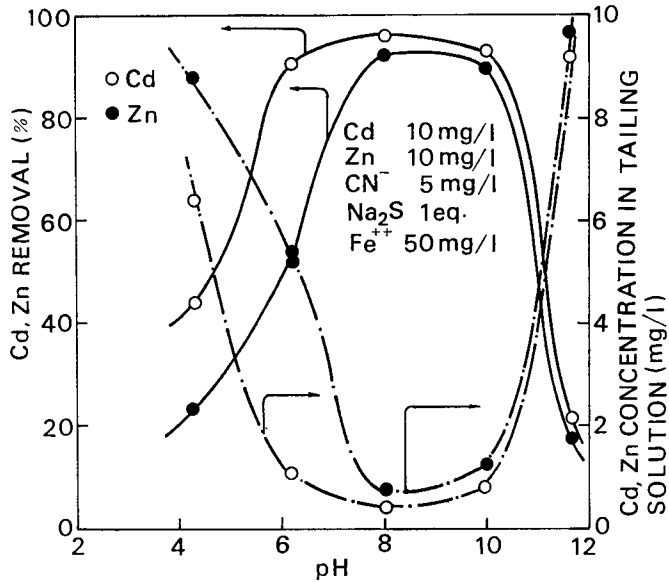


Fig. 4. Effect of pH on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with both ferrous salts and sodium oleate.

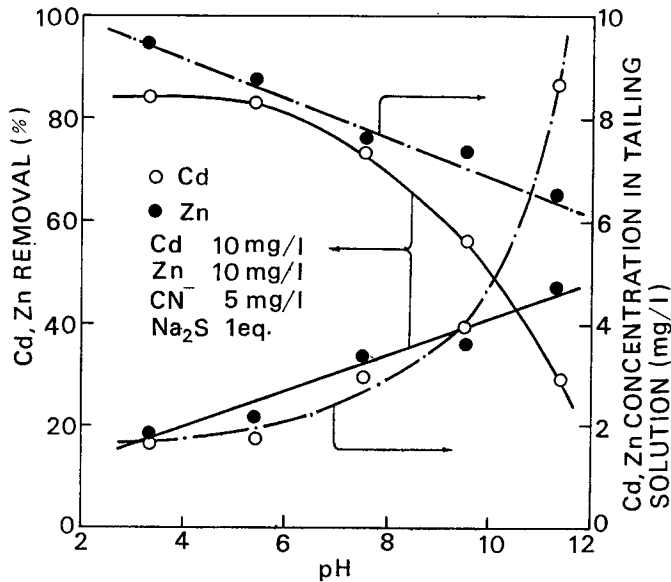


Fig. 5. Effect of pH on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with both sodium sulphide and sodium oleate.

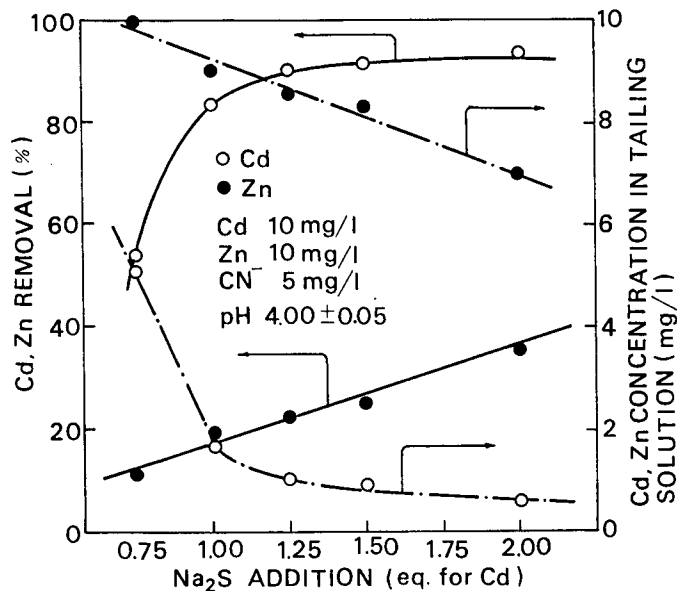


Fig. 6. Effect of the pretreatment by the addition of sodium sulphide on the removal of Cd-CN and Zn-CN complexes by the precipitation-flotation method with sodium oleate.

can be seen from Fig. 6, the removal of cadmium was 90% through the addition of sodium sulphide of over 1.25 equivalents, and the concentration of cadmium in the tailing solution was under 1 mg/l. However, the removal of zinc increased with an increased addition of sodium sulphide. From these results, the optimum addition of sodium sulphide was about 1.25 equivalents.

Fig. 7 and 8 show the results obtained by using potassium ethyl xanthate as a collector. Fig. 7 shows the effect of pH on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with pretreatment by using sodium sulphide of 1 equivalent. In the case of using potassium ethyl xanthate as a collector, the removal of cadmium was about 90% within the relatively wide pH range of 5 to 10. However, it was observed that the removal of zinc increased with the increase of pH. From these results, the optimum pH value was about 5 in order to separate cadmium from zinc in synthesized waste cyanide water.

Fig. 8 shows the effect of the addition of sodium sulphide on the removal of Cd-CN and Zn-CN complexes by the precipitation-flotation method by varying the addition of potassium ethyl xanthate as a parameter. It was found that the removal of cadmium was less with an increased addition of sodium sulphide, and the removal of zinc increased. In the case of the addition of sodium sulphide of under 1.5 equivalents, the removal of cadmium increased with an increased addition of potas-

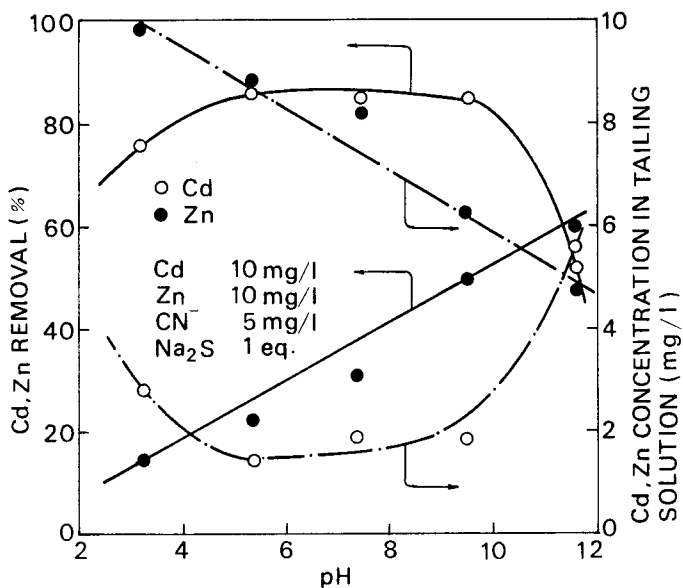


Fig. 7. Effect of pH on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with the pretreatment of sodium sulphide and with potassium ethyl xanthate.

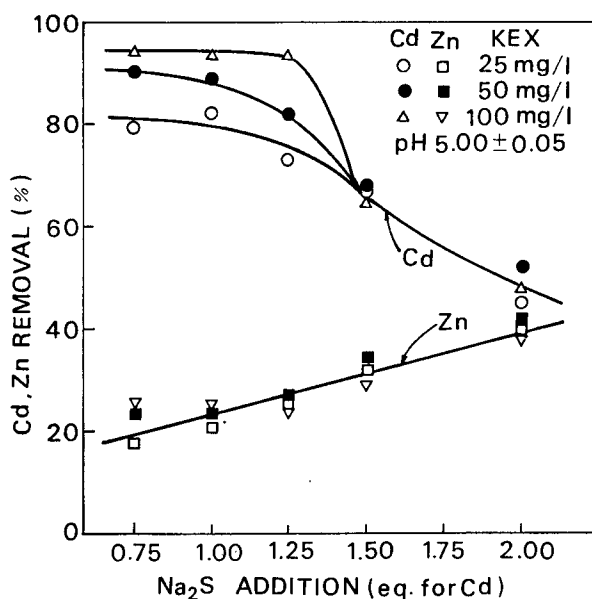


Fig. 8. Effect of the addition of sodium sulphide on the removal of Cd-CN and Zn-CN complexes by the precipitation-flotation method with potassium ethyl xanthate as a collector.

sium ethyl xanthate. Potassium ethyl xanthate did not have any effect on the removal of zinc. In the case of using potassium ethyl xanthate as a collector, the optimum addition of sodium sulphide and potassium ethyl xanthate were about 1 equivalent and over 50 mg/l, respectively.

3.2. Effect of Some Flocculants on Separation of Cadmium from Zinc in Synthesized Wastes Cyanide Water.

The improvement of the Cd removal was considered by carrying out flotation after the coagulation of the precipitates formed by the pretreatment of sodium sulphide. Two kinds of flocculants, Alkox and FC-80, were used in this experiment.

Fig. 9 shows the effect of pH on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method, with the pretreatment of sodium sulphide with Alkox as a flocculant and with sodium oleate as a collector. Fig. 9 shows that the removals of cadmium and zinc increase with the increase of pH values. In the acidic region of pH, the removal of cadmium tends to be less in comparison with no addition of Alkox. It can be said from the results obtained that such a non-ionic flocculant as Alkox is unfavorable for the differential separation of Cd-CN and Zn-CN complexes.

Fig. 10 shows the results in the case of the addition of FC-80 of 5 mg/l as a flocculant. By adding FC-80, the removal of cadmium was 97% within the relatively

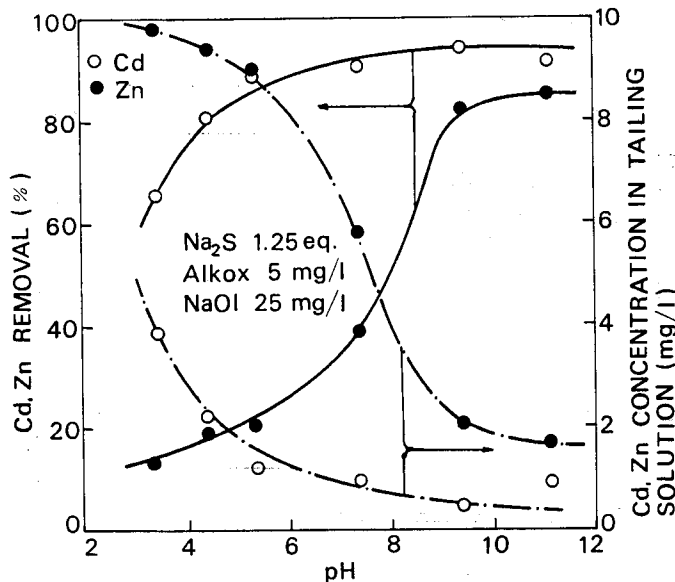


Fig. 9. Effect of pH on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with the pretreatment of sodium sulphide, with Alkox as a flocculant and with sodium oleate as a collector.

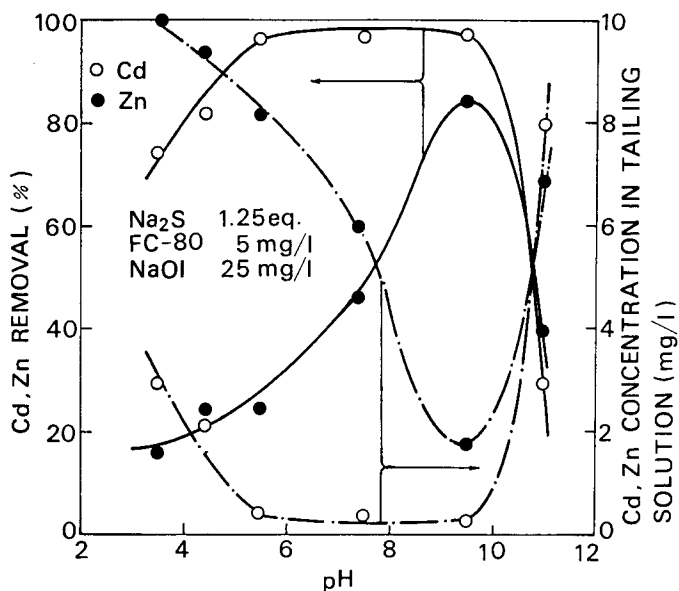


Fig. 10. Effect of pH on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with the pretreatment of sodium sulphide, with FC-80 as a flocculant and with sodium oleate as a collector.

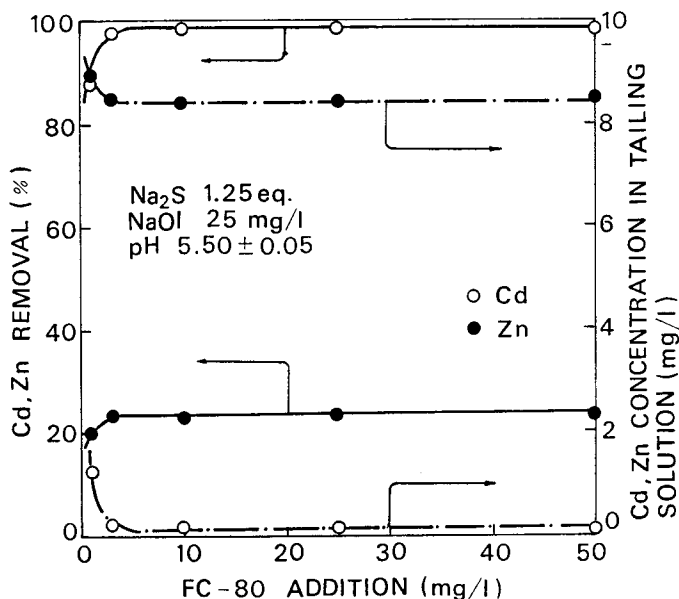


Fig. 11. Effect of the addition of FC-80 on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with the pretreatment of sodium sulphide and with sodium oleate as a collector.

wide pH range of 5.5 to 10.0 and the concentration of cadmium in the tailing solution was 0.3 mg/l. From the results obtained, the pH value for the differential separation of Cd-CN and Zn-CN complexes is about 5.5.

Fig. 11 shows the effect of the addition of FC-80. In this case, the pH value was constant at 5.5. Fig. 11 indicates that by adding FC-80 of over 5 mg/l, the removals of cadmium and zinc are 97% and 24%, respectively. FC-80 was effective for the separation of these metal cyanide complexes and the addition of FC-80 was sufficient in 5 mg/l.

3.3. Effect of Hydrogen Peroxide on Separation of Cadmium from Zinc in Synthesized Waste Cyanide Water by Precipitation-Flotation Method.

From the results obtained up to the previous sections, it was found that cadmium in a solution containing Cd-CN and Zn-CN complexes was selectively floated by using such an organic cationic flocculant as FC-80 and sodium oleate as a collector. In this section, the complete removal of zinc in the tailing solution was considered.

The authors had found the pretreatment of hydrogen peroxide was effective for the removal of the Zn-CN complex⁹⁾. Prior to the precipitation-flotation tests, a series of the precipitation tests was carried out with the addition of hydrogen peroxide and ferrous sulphate. A typical example of the results is shown in Fig. 12.

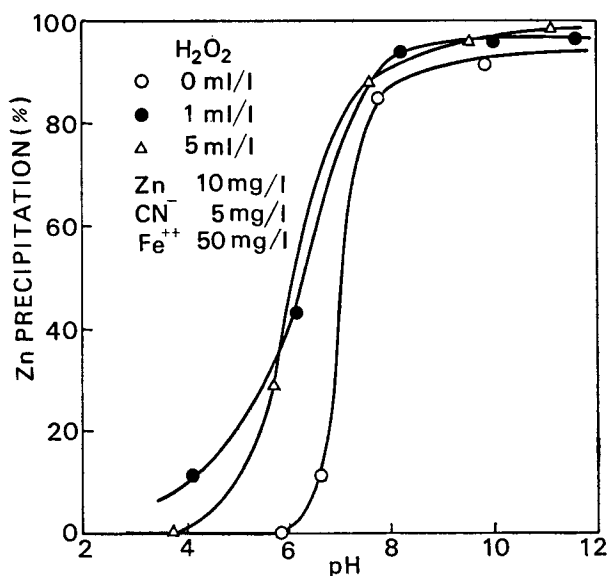


Fig. 12. Effect of pH on the precipitation of zinc in the presence of both hydrogen peroxide and ferrous ions from the solution containing Zn 10 mg/l and CN⁻ 5 mg/l.

In this particular case, the pretreatment was done at pH 10.5 for 20 minutes by adding a given amount of hydrogen peroxide to the test solution containing Zn 10 mg/l and CN^- 5 mg/l. Then, the precipitation tests were done with various pH values by adding 50 mg/l Fe(III) to the solution. As can be seen in Fig. 12, the precipitation of zinc was over 95% at the pH range of over 8.0 by means of pretreatment with the addition of hydrogen peroxide and the use of ferrous sulphate as a precipitant.

Based on the results obtained above, the precipitation-flotation test was carried out using sodium oleate as a collector at various pH values by applying the pretreatment method with hydrogen peroxide. As shown in Fig. 13, the Zn removal was about 90% at the pH range of 8.0 to 10.0. The removal of CN^- was 98% plus at all pH ranges. Fig. 13 indicates that cyanide ions were removed completely. However, it does not necessarily mean removal through flotation. In this case, cyanides may be removed as CNO^- or HCO_3^- which were formed through the decomposition by adding hydrogen peroxide.

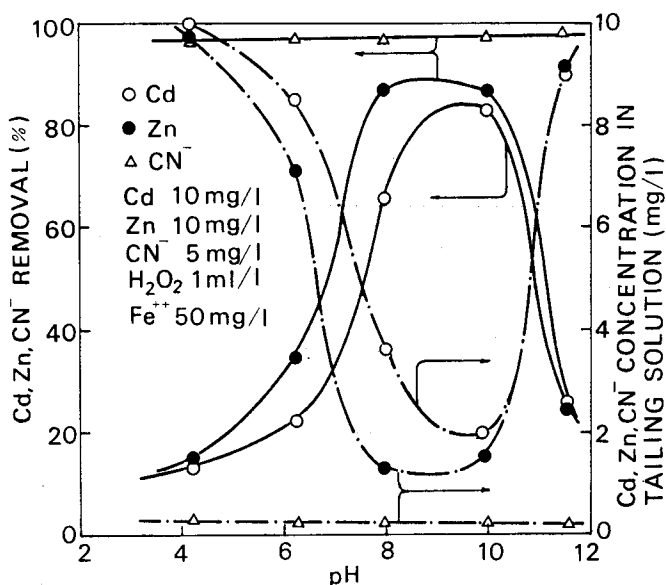


Fig. 13. Effect of pH with the addition of hydrogen peroxide on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method.

3.4. Differential Separation of Cadmium Zinc in Synthesized Waste Cyanide Water by Precipitation-Flotation Method.

Based on the results obtained from the previous sections, the differential separation of cadmium from zinc in synthesized waste cyanide water was examined by the

precipitation-flotation method.

A differential flotation test without any flocculant was carried out according to a flowsheet shown in Fig. 14. The results obtained are tabulated in Table 1. As can be seen in Table 1, the removal of Cd in the first flotation stage was about 91%. By treating the resultant solution with hydrogen peroxide in the second stage, the removal of Zn was about 80% and the cumulative removal of CN⁻ was about 93%. These results clearly suggest that the separation of cadmium from zinc in synthesized waste cyanide water according to the flowsheet shown in Fig. 14 is certainly successful.

Fig. 15 presents the flowsheet for the differential separation with such a flocculant as FC-80. Table 2 shows the flotation results. The removal of Cd in Froth 1 was 97% and the removal of Zn in Froth a was 70.8%. The concentrations of Cd, Zn

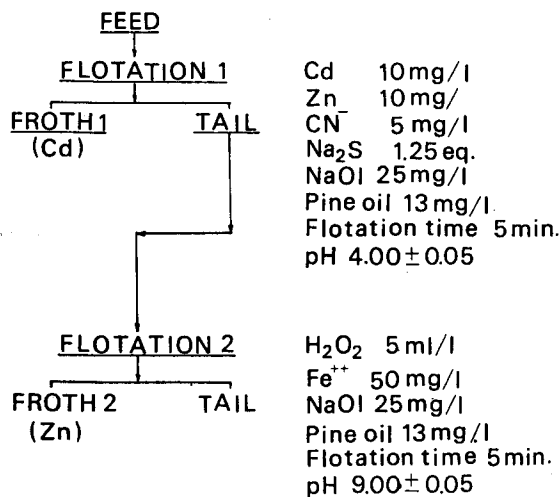


Fig. 14. Flowsheet with the pretreatment of sodium sulphide in the first stage and hydrogen peroxide in the second stage for the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method without the addition of any flocculant.

Table 1. Results of the differential flotation with the pretreatment of sodium sulphide in the first stage and hydrogen peroxide in the second stage.

PRODUCT	CONCENTRATION (mg/l)			REMOVAL (%)		
	Cd	Zn	CN ⁻	Cd	Zn	CN ⁻
FEED	10.00	10.00	5.00	100.00	100.00	100.00
FROTH 1	56.51	10.90	25.28	91.56	15.81	73.32
FROTH 2	6.84	38.99	4.87	7.57	80.01	19.99
TAIL	0.12	0.64	0.52	0.87	4.18	6.69

and CN^- in the final tailing solutions was 0.02 mg/l, 0.51 mg/l and 0.08 mg/l, respectively. These results are in conformity with the concentrations allowed by the law on the prevention of water pollution in Japan.

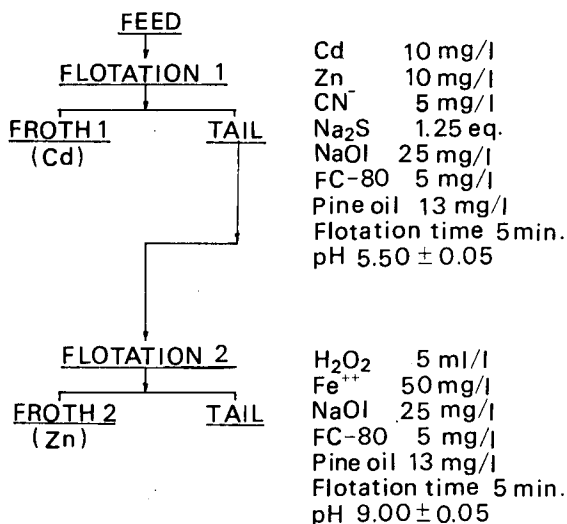


Fig. 15. Flowsheet with the pretreatment of sodium sulphide in the first stage and hydrogen peroxide in the second stage for the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation-flotation method with FC-80 as a flocculant.

Table 2. Results of the differential flotation with FC-80 as a flocculant.

PRODUCT	CONCENTRATION (mg/l)			REMOVAL (%)		
	Cd	Zn	CN^-	Cd	Zn	CN^-
FEED	10.00	10.00	5.00	100.00	100.00	100.00
FROTH 1	86.84	22.54	23.14	97.69	25.36	52.03
FROTH 2	1.62	53.18	17.55	2.16	70.80	46.71
TAIL 1	0.02	0.51	0.08	0.15	3.84	1.21

4. Conclusions

This study deals with the separation of cadmium from zinc in synthesized waste cyanide water and the simultaneous removal of cyanide by a precipitation-flotation method.

For the flotation removal of these substances, it was necessary to decompose the metal cyanide complexes prior to the flotation separation. The cadmium cyanide complexes were effectively decomposed by the addition of sodium sulphide, while the zinc cyanide complexes were decomposed by using hydrogen peroxide. In this

case, the organic cationic flocculant FC-80 was particularly effective for the removal of cadmium in synthesized waste cyanide water.

Based on the fundamental experiments, flowsheets were presented for the flotation separation of cadmium from zinc in synthesized waste cyanide water, showing a satisfactory separation of these metals.

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