

## A Study on the Separation of Cadmium from Zinc in Synthesized Waste Cyanide Water by Precipitation Method

By

Yoshitaka NAKAHIRO\*, Shigeharu NAKACHI\*, Kensaku MURAKAWA\*\*  
and Takahide WAKAMATSU

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### Abstract

The present study deals with the applicability of a precipitation method for the differential separation of Cd-CN and Zn-CN complexes in synthesized waste water.

In order to separate cadmium from zinc in synthesized waste cyanide water by the precipitation method, it was necessary to decompose the metal cyanide complexes prior to the precipitation treatment. From a series of tests, it was found that the pretreatment by the addition of sodium sulphide was effective for the selective precipitation of the Cd-CN complexes. On the other hand, the Zn-CN complexes were decomposed by the pretreatment of hydrogen peroxide, and then the zinc and cyanide ions were simultaneously precipitated by this method.

This method being applied, it was found that the differential separation of the constituting metals was effectively achieved by this method.

### 1. Introduction

Waste water solutions from mining and electroplating industries often contain harmful anions such as cyanide, chloride and fluoride. Generally, heavy metal ions form various complexes with cyanide as well as other complexing agents. When sodium cyanide is used as a depressant in the flotation of mineral separation, cyanides are usually contained in waste water besides heavy metal ions. For example, the waste water disposed from Pb/Zn flotation plants contains harmful heavy metal ions such as zinc, cadmium and lead besides cyanide ions. Such a kind of waste water treatment possesses many difficulties for this reason.

The authors had found that a precipitation-flotation method was successfully applicable for the removal of Cd-CN<sup>1)</sup>, Cu-CN<sup>2)</sup> and Zn-CN complexes<sup>3)</sup> from synthesized waste solutions. However, the differential separation of the constituting metals by this method has been thought to be very difficult when the waste

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\* Department of Mineral Science and Technology

\*\* Sumitomo Metal Industries Ltd.

solutions contain cyanides. The separation of cadmium from copper in synthesized waste cyanide water by a precipitation-flotation method had been examined by the authors and was found to be satisfactory<sup>4)</sup>.

In the present study, the applicability of the differential separation of cadmium from zinc in synthesized waste cyanide water was examined by the precipitation method. If the applicability of this method for the separation is promising, each of the sludges recovered is able to be reutilized. Thus, it will be possible that the treatment of such waste water can be carried out by the closed system.

## 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. The addition of cyanide ion concentration was usually 5 mg/l. An aqueous solution of ferrous sulphate containing 50 mg/l Fe(II) was used as a precipitant. Sodium sulphide was used as another precipitant for cadmium. All the chemicals mentioned above were of a reagent grade. A hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub> 30% pure) was used together with ferrous sulphate to decompose the metal cyanide complexes. The adjustment of pH was made either with sulphuric acid or sodium hydroxide.

The effect of pH on the precipitation of the Cd-CN and Zn-CN complexes was examined for the test solution containing cyanide ions of various concentrations. The addition of cyanide ions was 0, 5 and 10 mg/l, respectively. An aqueous solution of ferrous sulphate containing 50 mg/l Fe(II) was added to the test solutions, and then the pH was adjusted to the desired values. After the completion of precipitation, the precipitates were 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 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 Standard<sup>9)</sup>. An aliquot of solution was acidified with phosphoric acid, and then ethylenediaminetetraacetic acid was added to the solution. The solution was subjected to distillation in order to decompose the metal cyanide complexes. Released cyanide ions were collected in a distilled solution. The concentration of cyanide ions in the solution was determined electrochemically, using a cyanide electrode.

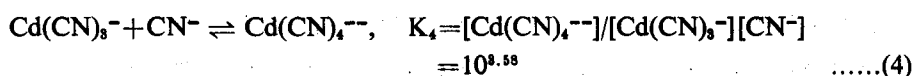
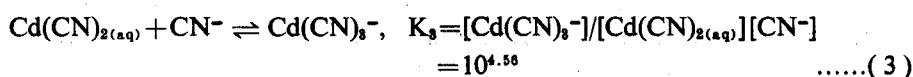
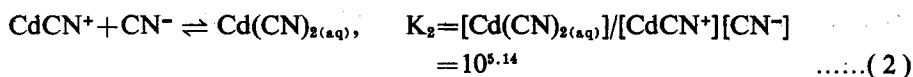
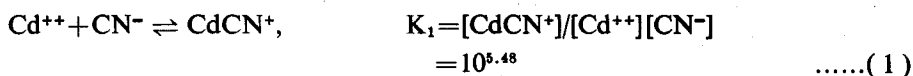
In a series of precipitation tests with sodium sulphide, sodium sulphide was added to the test solutions containing Cd-CN and Zn-CN complexes for decomposition and precipitation purposes. Then, the adjustment of pH was carried out. In another test, ferrous sulphate was used together with sodium sulphide. In this case, ferrous sulphate was added 50 mg/l Fe(II) after decomposing the metal cyanide complexes with sodium sulphide. The procedures of analysis were carried out in the same manner as mentioned above.

The effect of hydrogen peroxide on the precipitation was examined for the test solutions containing Cd-CN and Zn-CN complexes. A predetermined amount of hydrogen peroxide was added to the test solutions of pH 10.5. The solution was kept at an 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 and analysis were carried out in the same manner as mentioned above.

### 3. Thermodynamic Consideration of the Precipitation of Cadmium and Zinc from Cyanide Solutions

The difficulty of the removal of cadmium, zinc etc. from a waste cyanide solution by a precipitation-flotation method may be attributed to the poor precipitation ability of those metals in the cyanide solutions. Taking the systems of Cd-CN-H<sub>2</sub>O and Zn-CN-H<sub>2</sub>O, thermodynamic considerations were made with regard to the effect of cyanide ions on the precipitation of cadmium and zinc hydroxides.

First, the effect of cyanide ions in waste water was examined concerning the precipitation of cadmium hydroxide. The formation constants of the cadmium cyanide complexes were reported as follows<sup>6)</sup>:



As recognized in the above formation constants, cadmium exists as cadmium ions beyond pCN 7, whereas cadmium cyanide complexes become stable at low pCN

ranges. A mono-cyano complex of cadmium is stable only at low pCN levels. The presence of an excessive amount of cyanide ions in the solution causes an undesirable influence on the precipitation formation of cadmium hydroxide.

In a cyanide solution, cadmium exists as simple ions, cyano- and hydroxo-compounds. The mass balance on cadmium gives:

$$T_{Cd} = [Cd^{++}] + [CdCN^+] + [Cd(CN)_{2(aq)}] + [Cd(CN)_3^-] + [Cd(CN)_4^{--}] \\ + [CdOH^+] + [Cd(OH)_{2(aq)}] + [Cd(OH)_3^-] + [Cd(OH)_4^{--}] \quad \dots\dots (5)$$

where  $T_{Cd}$  is the total amount of cadmium in the solution.

The proton condition and the ionization of water is expressed as

$$[H^+] = [OH^-] + [CdOH^+] + 2[Cd(OH)_{2(aq)}] + 3[Cd(OH)_3^-] \\ + 4[Cd(OH)_4^{--}] \quad \dots\dots (6)$$

$$K_w = [H^+][OH^-] = 10^{-14} \quad \dots\dots (7)$$

From these equations, we can calculate the values of  $[H^+]$  and  $[OH^-]$ . The stability domain of the  $Cd(OH)_2$  precipitates can be determined by the maximum values of  $T_{Cd}$  for the solution.

The limitation for the precipitation of  $Cd(OH)_{2(s)}$  can be calculated from the  $K_{s2}$  value<sup>7)</sup>, as shown in Eq. (8).

$$[Cd(OH)_{2(aq)}] \geq 10^{-5.87} \quad \dots\dots (8)$$

On the other hand,  $T_{Cd}$  for the solution under the given values of pCN and pH is able to be calculated, because the stabilities of cadmium cyanide complexes are the functions of pCN and pH.

The relationship between  $\log T_{Cd}$  and pH is shown in Fig. 1 as a parameter of pCN. The stability domain is reduced greatly by the increase of cyanide concentration. At a higher cyanide concentration, the precipitation formation of  $Cd(OH)_{2(s)}$  becomes more difficult.

As considered above, from a thermodynamic point of view, it is thought that the removal of cadmium in waste cyanide water becomes difficult even at low concentrations of cyanide ions.

It is possible to carry out a thermodynamic consideration of the Zn-CN- $H_2O$  system in the same manner as mentioned above. The formation constant of the zinc cyanide complexes were reported as follows<sup>9)</sup>:



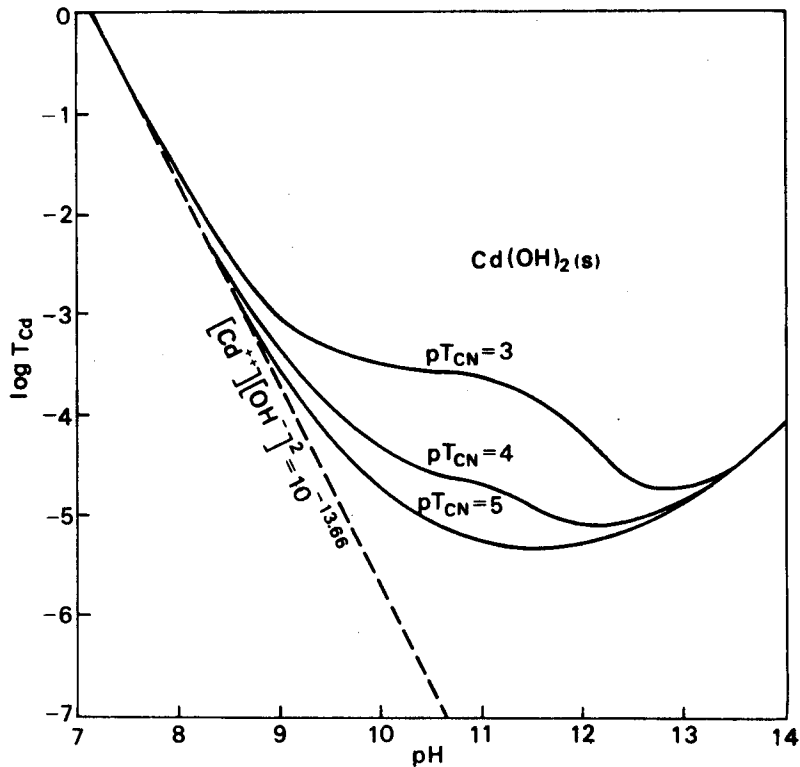


Fig. 1. Domain of the stability of cadmium hydroxide at different pCN levels.

As recognized in the above formation constants, zinc exists as zinc ions beyond pCN 8. Whereas zinc cyanide complexes become stable at low pCN ranges, a mono-cyano complex of zinc is stable only at low pCN levels. The presence of an excessive amount of cyanide ions in the solution causes an undesirable influence on the precipitation formation of zinc hydroxide.

In a cyanide solution, zinc exists as simple ions, cyano- and hydroxo-compounds. The mass balance on zinc gives:

$$T_{Zn} = [Zn^{2+}] + [ZnCN^+] + [Zn(CN)_2(aq)] + [Zn(CN)_3^-] + [Zn(CN)_4^{--}] + [ZnOH^+] + [Zn(OH)_2(aq)] + [Zn(OH)_3^-] + [Zn(OH)_4^{--}] \quad \dots\dots(13)$$

where  $T_{Zn}$  is the total amount of zinc in the solution.

The proton condition and the ionization of water is expressed as

$$[H^+] = [OH^-] + [ZnOH^+] + 2[Zn(OH)_2(aq)] + 3[Zn(OH)_3^-] + 4[Zn(OH)_4^{--}] \quad \dots\dots(14)$$

By combining these equations with Eq. (7), we can calculate the values of  $[H^+]$  and  $[OH^-]$ . The stability domain of  $Zn(OH)_2$  precipitates can be determined by the

maximum values of  $T_{Zn}$  for the solution.

The limitation for the precipitation of  $Zn(OH)_2(s)$  can be calculated from the  $K_{S2}$  value<sup>9)</sup>, as shown in Eq. (15).

$$[Zn(OH)_2(aq)] \geq 10^{-7.0} \quad \dots\dots(15)$$

On the other hand,  $T_{Zn}$  for the solution under the given values of pCN and pH is able to be calculated, because the stabilities of zinc cyanide complexes are the functions of pCN and pH.

The relationship between  $\log T_{Zn}$  and pH is shown in Fig. 2 as a parameter of pCN. The stability domain is reduced greatly by the increase of cyanide concentration. At a higher cyanide concentration, the precipitation formation of  $Zn(OH)_2(s)$  becomes more difficult.

As considered above, from a thermodynamic point of view, it is thought that the removal of cadmium and zinc in waste cyanide water becomes difficult even at low concentrations of cyanide ions.

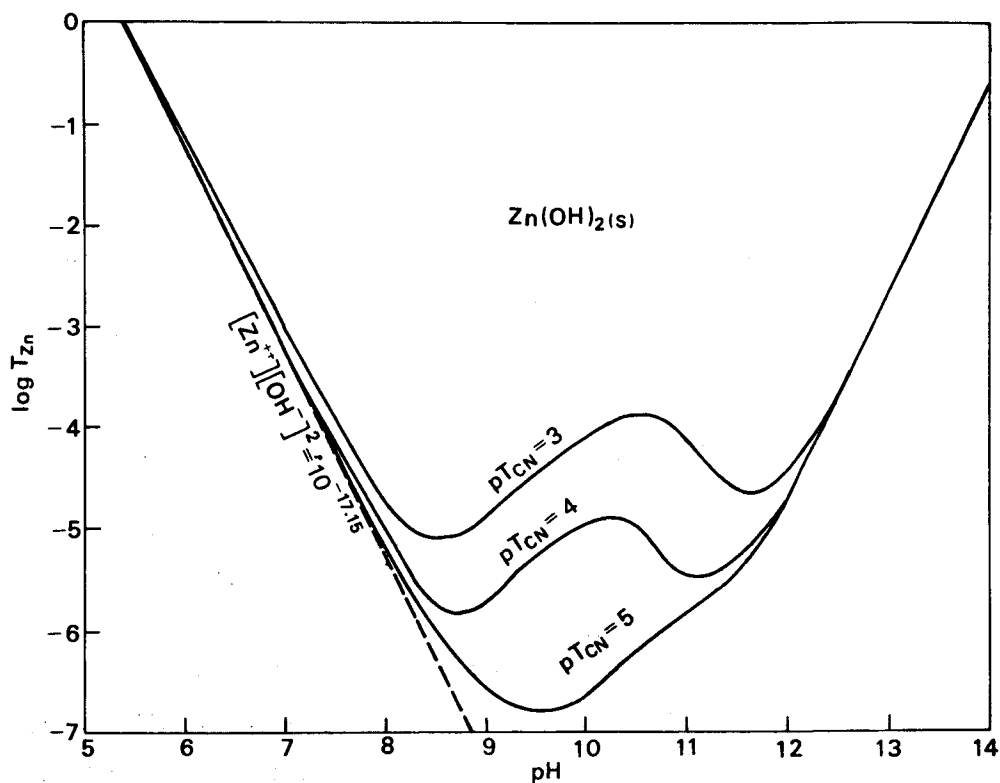


Fig. 2. Domain of the stability of zinc hydroxide at different pCN levels.

#### 4. Experimental Results and Discussion

##### 4.1 Effect of $\text{CN}^-$ Concentration and pH on Precipitation of Cadmium and Zinc.

A series of precipitation tests was carried out by varying the addition of cyanide ions in the test solutions, in order to examine the effect of pH for the precipitation of cadmium and zinc. The results obtained are shown in Fig. 3. It is recognized that the formation of cadmium precipitation shifts to the alkaline region with the increase of cyanide concentration in the test solutions. On the other hand, in the presence of cyanide in the test solutions, the precipitation of zinc decreases with an increase of cyanide concentration.

The effect of the Fe(II) addition was examined in the test solutions containing Cd 10 mg/l, Zn 10 mg/l and  $\text{CN}^-$  5 mg/l under the pH values of 8.0 and 9.0. The results obtained are given in Fig. 4. As shown in Fig. 4, the effect of the Fe(II) addition was found in the case of pH 9.0. In this case, the precipitations of Cd, Zn, and  $\text{CN}^-$  increased by increasing the amount of the Fe(II) addition. However, the effect of the Fe(II) addition in the pH of 8.0 was not considerable.

As can be seen from the above results, it was difficult to separate cadmium from zinc in synthesized waste cyanide water only by the precipitation method with the Fe(II) addition and the pH adjustment.

##### 4.2 Effect of Sodium Sulphide on Separation of Cadmium from Zinc in Synthesized Waste Cyanide Water by Precipitation Method.

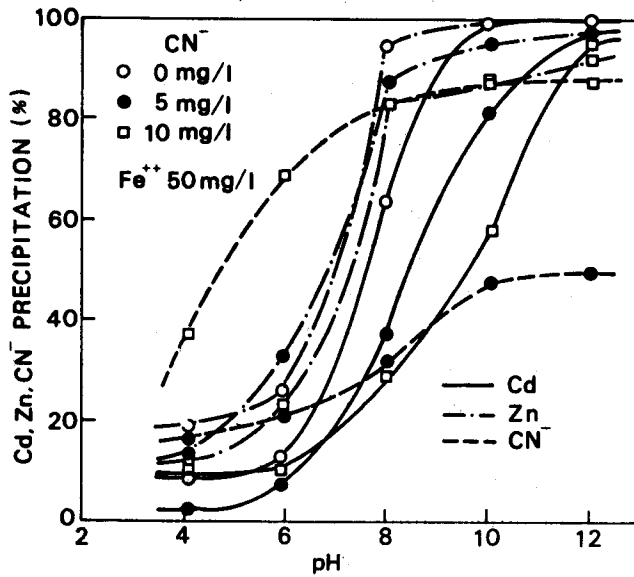


Fig. 3. Effect of pH on the precipitation of Cd, Zn, and  $\text{CN}^-$  with ferrous salt.

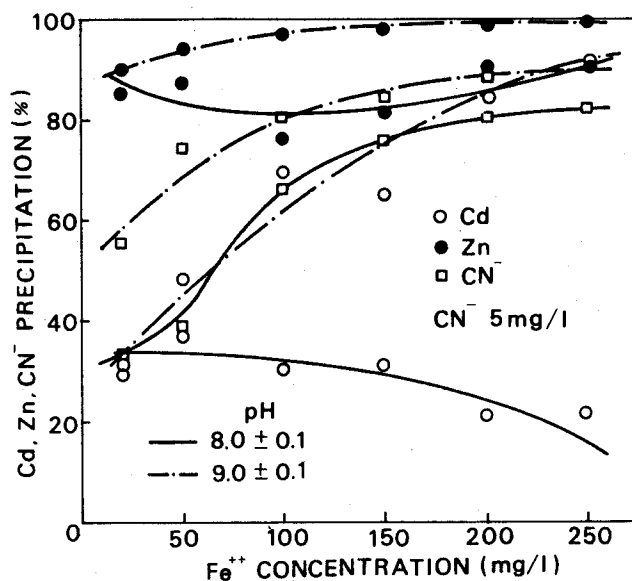


Fig. 4. Effect of added concentrations of ferrous salt on the precipitation of Cd, Zn, and  $\text{CN}^-$  at the pH values of 8.0 and 9.0.

One of the authors has observed that sodium sulphide is effective for the removal of Cd-CN complexes in waste water<sup>10)</sup>. Accordingly, the effect of sodium sulphide was examined in order to precipitate Cd-CN complexes selectively.

The reaction for the decomposition of Cd-CN complexes with sodium sulphide would be:



The above reaction is known to proceed quantitatively<sup>11)</sup>. Compared to the stability of the cyano-complexes of cadmium, the stability of cadmium sulphide is far greater, because the solubility product of cadmium sulphide is very low.

The precipitation characteristics of Cd-CN and Zn-CN complexes were examined with sodium sulphide. Fig. 5 shows the effect of pH on the precipitation of Cd, Zn and  $\text{CN}^-$  by the addition of sodium sulphide without ferrous salt. As shown in Fig. 5, the precipitation of cadmium was complete in the pH range below 10.0 when two equivalents of  $\text{Na}_2\text{S}$  were added. In the case of the addition of one equivalent of  $\text{Na}_2\text{S}$ , the precipitation of cadmium was about 85% over the pH values tested. On the other hand, the precipitation of zinc was about 10% in the acidic region of pH below 6.0 in the case of the addition of one equivalent of  $\text{Na}_2\text{S}$ . In the range of pH above 6.0, the precipitation of zinc tends to increase.

As can be seen from the above results, it is possible to separate Cd-CN complexes



from Zn-CN complexes in the range of pH below 6.0, because Cd-CN complexes are selectively decomposed by sodium sulphide under these conditions. In this case, cyanide ions were not removed from the solution.

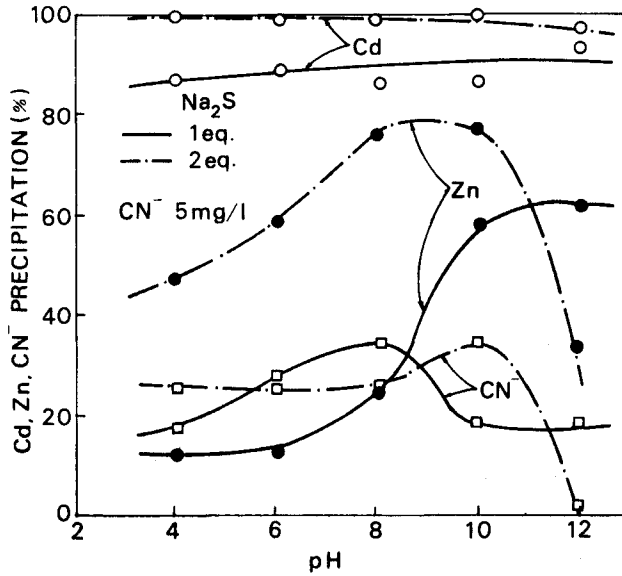


Fig. 5. Effect of pH on the precipitation of Cd, Zn, and CN<sup>-</sup> by the addition of sodium sulphide without ferrous salt.

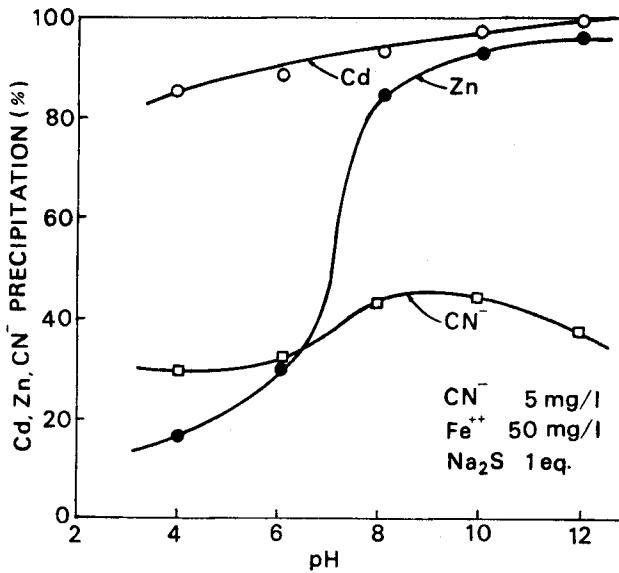


Fig. 6. Effect of pH on the precipitation of Cd, Zn, and CN<sup>-</sup> by the addition of both sodium sulphide and ferrous salt.

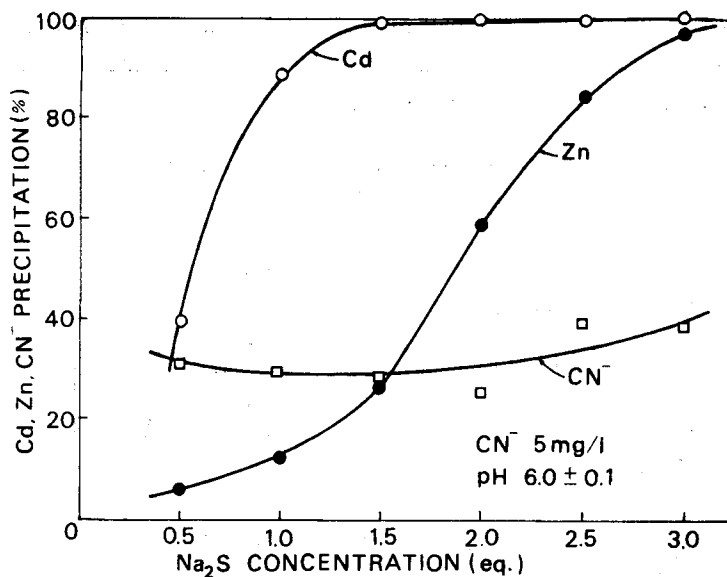


Fig. 7. Effect of added concentrations of sodium sulphide on the precipitation of Cd, Zn, and CN<sup>-</sup> at the fixed pH value of 6.0.

Fig. 6 shows the effect of pH on the precipitation of Cd, Zn, and CN<sup>-</sup> by the addition of both sodium sulphide and ferrous salt. In the case of adding sodium sulphide together with ferrous salt, the precipitation of cadmium increases by increasing the pH values. Also, the behavior of the zinc precipitation is the same as that of cadmium. Thus, the addition of ferrous salt is undesirable in order to separate cadmium from zinc in waste cyanide water. The addition of ferrous salt is not effective for the removal of cyanide ions.

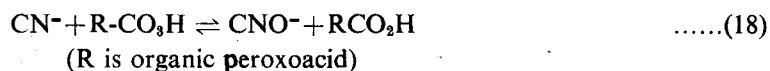
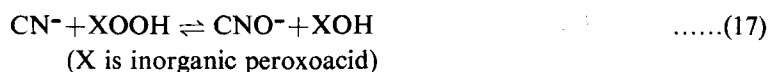
Fig. 7 shows the effect of the addition of sodium sulphide on the precipitation of Cd, Zn, and CN<sup>-</sup> at the fixed pH value of 6.0. As can be seen in Fig. 7, the precipitations of Cd and Zn tend to increase considerably with an increase of the Na<sub>2</sub>S addition. On the other hand, the precipitation of CN<sup>-</sup> is 30 to 40% to show the constant values. From these results, the optimum addition of sodium sulphide is 1 to 1.5 equivalents in order to separate Cd-CN complexes from Zn-CN complexes.

#### 4.3 Effect of Hydrogen Peroxide on Separation of Cadmium from Zinc in Synthesized Waste Cyanide Water by Precipitation Method.

As can be seen from the results obtained in the previous sections, it is anticipated that the precipitation separation of cadmium from zinc in synthesized waste cyanide water may be achieved at the appropriate pH value by the precipitation with sodium sulphide. This section is concerned about the removal of the Zn-CN complexes which were retained in the solution after the Cd-CN complexes were removed by the

precipitation method with sodium sulphide.

In order to assist the decomposition of zinc cyanide complexes, the effect of pretreatment with hydrogen peroxide was examined. In regard to this, J.P. Zumbunn studied the decomposition of heavy metal cyanide complexes with peroxides<sup>12)</sup>. He found that the cyanide complexes of metals, such as zinc, copper, nickel and silver were easily decomposed by using the inorganic or organic peroxyacid which possesses the -OOH group within the molecule. He also mentioned that  $CN^-$  was finally oxidized to  $CNO^-$  without the addition of any specific catalysts. In this study, hydrogen peroxide was used as a reagent for the decomposition of zinc cyanide complexes.



A series of precipitation tests was carried out with the addition of hydrogen peroxide and ferrous sulphate. Fig. 8 shows the results which were obtained with and without 5 mg/l of hydrogen peroxide. In this case, ferrous sulphate was added 50 mg/l. As shown in Fig. 8, it was found that the effect of hydrogen peroxide was considerable for the removal of cyanide ions. However, the precipitation of

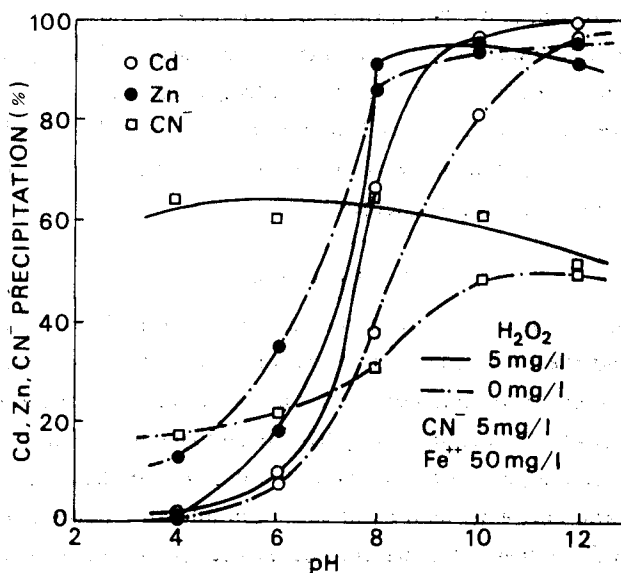


Fig. 8. Effect of pH on the precipitation of Cd, Zn, and  $CN^-$  with and without hydrogen peroxide.

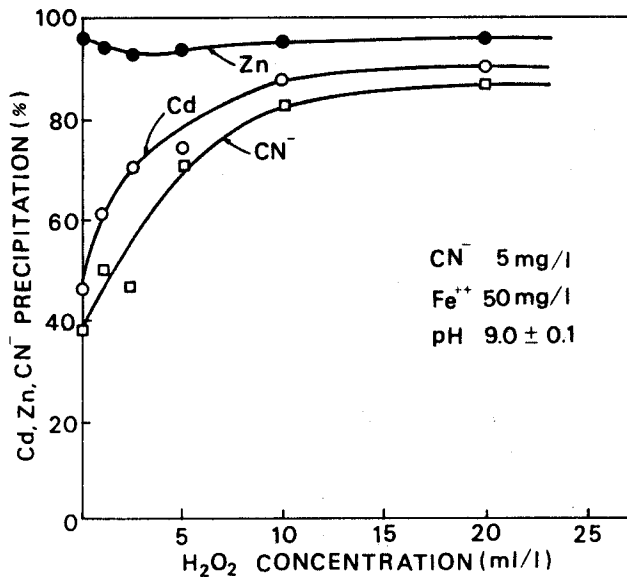


Fig. 9. Effect of added concentrations of hydrogen peroxide on the precipitation of Cd, Zn, and CN<sup>-</sup> at the fixed pH value of 9.0.

zinc with the addition of hydrogen peroxide showed similar results to those without any addition of hydrogen peroxide.

Fig. 9 shows the effect of added concentrations of hydrogen peroxide on the precipitation of Cd, Zn, and CN<sup>-</sup> at the fixed pH value of 9.0. As shown in Fig. 9, the precipitation of zinc was over 95% and the precipitation of Cd and CN<sup>-</sup> increased considerably with an increase of the added hydrogen peroxide.

From the above results, it was found that zinc cyanide complexes were decomposed by pretreatment with hydrogen peroxide to remove simultaneously both Zn and CN<sup>-</sup> by the precipitation method.

## 5. 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 method.

First of all, thermodynamic considerations were made on the effect of cyanide ions on the precipitations of cadmium hydroxide and zinc hydroxide. As recognized in the distribution diagrams of Cd-CN and Zn-CN complexes as parameters of pCN, cadmium and zinc exist as ions of cadmium and zinc beyond pCN 7 and 7.5, respectively. Both of these cyanide complexes become stable at low pCN ranges. Mono-cyano complexes of cadmium and zinc are stable only at low pCN levels. The presence of an excessive amount of cyanide ions in the solution causes an undesir-

able influence on the precipitation formation of  $\text{Cd}(\text{OH})_{2(s)}$  and  $\text{Zn}(\text{OH})_{2(s)}$ . On the other hand, as recognized from the relationships between  $\log T_{\text{Cd}}$  or  $T_{\text{Zn}}$  and pH, the stability domains of these metal hydroxides are reduced greatly by the increase of cyanide concentration. At a higher cyanide concentration, the precipitation formations of  $\text{Cd}(\text{OH})_{2(s)}$  and  $\text{Zn}(\text{OH})_{2(s)}$  become more difficult.

As considered from a thermodynamic point of view, it was found that the precipitations of cadmium and zinc in waste cyanide water became difficult even at low concentrations of cyanide ions.

Next, the effect of pretreatment with sodium sulphide was examined on the separation of cadmium from zinc in synthesized waste cyanide water by the precipitation method. From the results obtained, it was possible to separate cadmium from zinc in synthesized waste cyanide water in the range of pH below 6.0. This was because the Cd-CN complexes were selectively decomposed by sodium sulphide under these conditions. In this case, cyanide ions were not removed from the solution by the precipitation method.

Furthermore, the effect of pretreatment with hydrogen peroxide was examined in order to remove the Zn-CN complexes which were retained in the solution after the Cd-CN complexes were removed by the precipitation method with sodium sulphide. From the results obtained, it was found that zinc cyanide complexes were effectively decomposed by pretreatment with hydrogen peroxide to remove simultaneously both zinc and cyanide ions.

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