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Studies on the Separation of Cadmium from Solutions by Foam Separation. II. Precipitate Flotation of Cadmium Hydroxide

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Abstract

Foam separation of cadmium in relation to pH from solutions of different metal concentrations was carried out by means of lauryl sulfate. The effect of inert salt on the removal of cadmium hydroxide and cadmium cations by adsorbing colloid floation was also studied. The precipitate flotation results reflect the precipitation of the metal in the form of a hydroxide. The precipitation pH values calculated are approximately those at which cadmium removal over 50% is obtained. The presence of electrolyte has a negative effect on the results of precipitate flotation of cadmium hydroxide and adsorbing colloid flotation of cadmium cations with lauryl sulfate.

INTRODUCTION

In an earlier paper the foam separation of cadmium from electrolytes by using lauryl sulfate and sodium soaps was characterized (*1*). It was found that ion flotation of cadmium in the form of a low-soluble precipitate, e.g., a cadmium soap, was effective. The studies have been extended to precipitate flotation of another nature. Attention has been drawn to the fact that one of the methods of removing cadmium ions from real solutions in the form of a sediment is precipitation of hydroxide. Precipitation itself is relatively simple, but the way of removing the sludges precipitated is a frequent problem. Therefore, a currant problem is the use of precipitate flotation of hydroxides to exclude the metals from solution. Among the studies published on this subject, the following may be recognized as basic. Rubin

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and Johnson (*2*) discussed this problem with respect to Fe and Cu. The anionic collector (sodium lauryl sulfate) and cationic collector (stearylamine) were used to remove both soluble and insoluble copper and iron species. Rubin and Lapp (*3, 4*) reported the effect of pH and other factors on the foam separation of lead and zinc using anionic surfactant–sodium lauryl sulfate as the collector. Rubin (*5*) described studies on the removal and use of hydrolyzed metals in foam separation. Bhattacharyya et al. (*6*) investigated the efficiency of chromium foam separation as a function of pH, collector concentration, and ionic strength. The results were related to the hydrolytic behavior of the metal.

Skrylev's group (*7, 8*) reported the results of precipitate flotation for several metals vs pH with the use of anionic collectors. Kobayashi (*9*) discussed the results of foam separation of cadmium vs pH and the effect of the nature of surfactants (anionic and cationic) and bentonite on flotation recovery.

However, in recent years the most systematic studies on precipitate flotation and adsorbing colloid flotation processes have been carried out by Wilson et al. (*10–14*). These studies mainly concern the flotation of $Fe(OH)_3$ and $Al(OH)_3$ and to some degree $Cd(OH)_2$ flotation. The effects of pH, ionic strength, and the nature of the ionic species on foam separation are reported. The author of this paper has also published the results of studies on Co, Ni, Cu, and Zn flotation at various pH and ionic strengths (*15–18*). In the present article, new information describing the cadmium precipitate flotation process is presented.

EXPERIMENTAL

Cd^{2+} solutions were used in the experiments. It came from analytically pure $3CdSO_4 \cdot 8H_2O$ produced by POCH Gliwice (Poland). The pH of the solutions was regulated by means of analytically pure NaOH, NH_4OH, and H_2SO_4 produced by POCH Gliwice. The collectors used were pure sodium lauryl sulfate (from BDH Laboratory Division, England) in propanol:water (1:1) solutions and pure Tween 80 (polyoxyethylene sorbitan monooleate) (from Koch Light Laboratories, Colnbrock, Buckes, England). The amount of lauryl sulfate used was 2×10^{-4} M/dm^3, and that of Tween 80 was 0.01% v/v.

Hydroxide suspension was prepared by precipitating $Cd(OH)_2$ with NaOH solution. After 12 h the collector was added to the suspension and floated. Precipitate flotation was carried out in a multibubble apparatus. The apparatus was a glass column 200 cm^3 in volume and 25 cm high, with a G-3 sinter at its bottom.

Adsorbing colloid flotation of cadmium cations by hydroxide from the suspension of 0.1 g $Cd(OH)_2$ in a 250 cm^3 solution at a concentration of 10^{-4} M/dm^3 Cd^{2+} was carried out.

The flotation effectiveness was calculated from determinations of cadmium in the initial suspension and in the residual suspension by use of the polarographic method (*1*).

RESULTS

The experiment results obtained are illustrated in Figs. 1–4. The amount of the metal removed as a function of the solution pH as regulated with NaOH or NH_4OH is presented in Fig. 1. Lauryl sulfate amounting to 2×10^{-4} M/dm^3, i.e., in a stoichiometric amount based on the concentration of Cd^{2+} in the solution prior to hydroxide precipitation, was used as the collector. Figure 1 also illustrates the relationship of the soluble form of cadmium in the suspension solution vs pH.

From an analysis of the flotation curves (1 and 2) it appears that near pH 7.5 a considerable increase in metal removal occurs. The pH at which 50% of the cadmium is obtained ($pH_{1/2}$) is ~8.9. However, at pH ~9.5, removal is nearly 85%. If the pH is further increased by adding NaOH, the

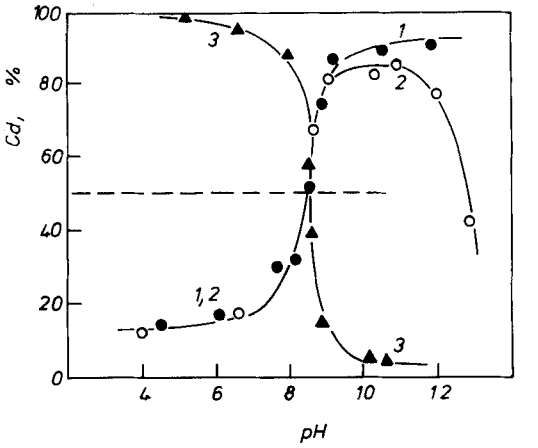

FIG. 1. Effect of solution pH on removal and precipitation of cadmium hydroxide from the solution. (1) Flotation from solutions at pH adjusted with NaOH, (2) flotation from solutions at pH adjusted with NH_4OH, and (3) soluble cadmium remaining in the solution of suspension.

efficiency of the flotation does not change (Curve 1). On the contrary, if the pH is increased above 11 by adding NH_4OH, a sharp decrease in cadmium removal is observed (Curve 2). From the course of precipitation of cadmium hydroxide with a sodium base (Curve 3) it can be seen that from pH of ~7.5 upward, a considerable decrease of cadmium in solution occurs, with close to 50% precipitation taking place at pH 8.9. A maximum (about 95%) is removed at pH ~9.5. It appears from a comparison of the flotation and precipitation curves that the pH of increased removal corresponds to an increasing amount of precipitated hydroxide. The pH of the highest removal corresponds to the highest precipitation of hydroxide.

Figure 2 illustrates the effectiveness of cadmium flotation as a pH function with the use of lauryl sulfate at a concentration of 2×10^{-4} M/dm^3 (Curve 1) or Tween 80 as collector at a concentration of 0.01% v/v (Curve 2). By analyzing the flotation curves it is concluded that their shapes are similar, i.e., with a pH increase the initial removal increases slightly and then rapidly, reaching about 90%. At that point a divergence of the flotation curves is observed which depends on the nature of the surface-active substance. When using lauryl sulfate a distinct removal increase above a pH of ~7.5 is observed, and at a higher pH with Tween 80. The maximum removal for these collectors is at a pH of ~9.5.

Figure 3(A) shows the influence of pH on cadmium flotation from solutions of different Cd^{2+} concentrations by means of lauryl sulfate at a concentration of 2×10^{-4} M/dm^3. As can be seen, the higher the metal concentration, the more the flotation curves are shifted toward lower pH

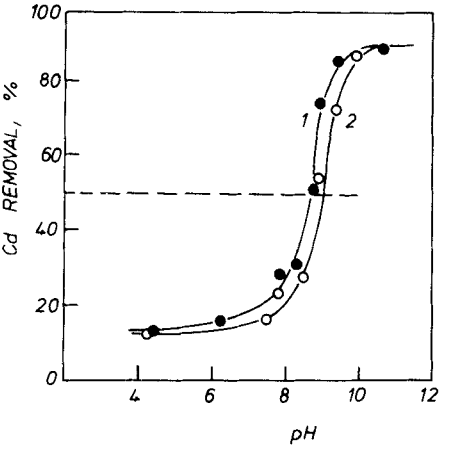

FIG. 2. Flotation of cadmium vs pH with (1) lauryl sulfate and (2) Tween 80.

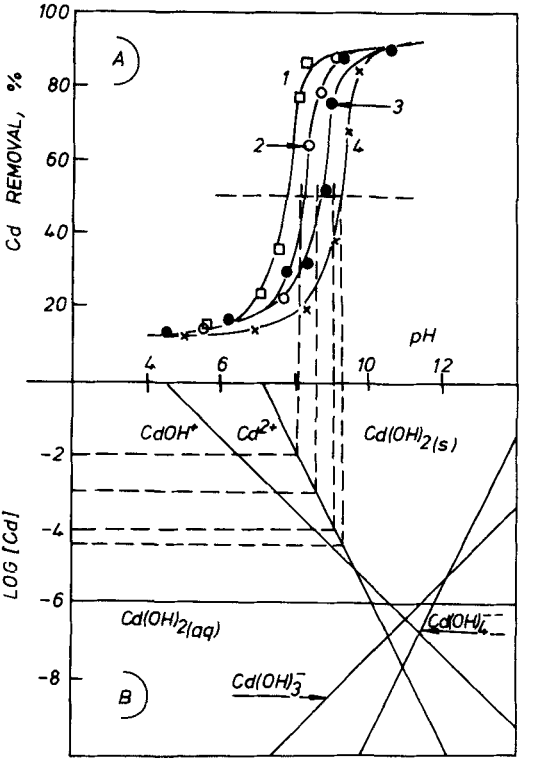

FIG. 3. (A) Flotation of cadmium vs pH from suspension at different metal concentrations: (1) 10^{-2}, (2) 10^{-3}, (3) 10^{-4}, and (4) 6×10^{-5} in M/dm^3. (B) Diagram of cadmium hydroxide solubility and of the occurrence of various forms of cadmium in relation to its concentration and pH.

values. For solutions with Cd^{2+} concentrations of 10^{-2}, 10^{-3}, 10^{-4}, and 6×10^{-5} M/dm^3, 50% removal occurs near pH 7.8, 8.4, 8.9, and 9.0, respectively, and the highest removal is obtained at pH 9.5 for all Cd^{2+} concentration values.

The influence of sodium sulfate concentration on cadmium removal is illustrated by the curves in Fig. 4. Curves 1 and 2 concern precipitate flotation of hydroxide at a constant pH of 9.9 by using Tween and lauryl sulfate, respectively, while Curve 3 characterizes adsorbing colloid flotation of Cd^{2+} by hydroxides with lauryl sulfate. From Fig. 4 it is seen that the effectiveness of precipitate flotation of hydroxide and adsorbing colloid flotation of Cd^{2+} using lauryl sulfate decreases as the electrolyte concentration increases. With an increase in sulfate concentration to 0.3 M/dm^3,

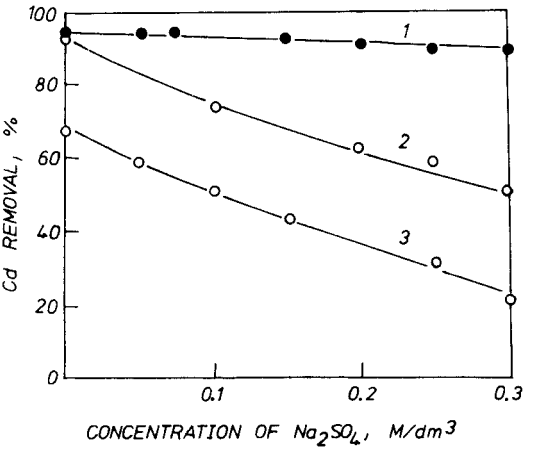

FIG. 4. Effect of sodium sulfate concentration on precipitate flotation of cadmium hydroxide results [(1) by using Tween 80, (2) with lauryl sulfate] and on cadmium cations removal by adsorbing colloid flotation [(3) with lauryl sulfate].

hydroxide removal decreases from about 95% to about 55%, and Cd^{2+} removal decreases from about 70 to 20%. However, by using the surface-active nonionic substance Tween 80, the negative effect of electrolyte on hydroxide removal, which is maintained over 90%, is not as distinct.

DISCUSSION

Figure 3(B) is a diagram of cadmium hydroxide solubility and of the occurrence of various forms of cadmium in relation to its concentration and pH. This diagram was plotted on the basis of calculations from the literature (*19, 20*).

By analyzing Figs. 1 and 2 it can be seen that the flotation curves reflect hydroxide precipitation. According to reaction (*21*)

$$Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2OH^-, \; pK = 13.66$$

if the hydroxide precipitation pH in relation to the metal concentration amounts to 6×10^{-5} M/dm^3, the hydroxide sediment should be precipitated at pH 9.28. If the Cd^{2+} concentration is 10^{-4} M/dm^3, the precipitation pH should be 9.2. For Cd^{2+} concentrations of 10^{-3} and 10^{-2} M/dm^3, the precipitation pH should be 8.7 and 8.2, respectively.

By analyzing the flotation curves (Fig. 3A) for different concentrations of the metal, it can be seen that a considerable increase of Cd^{2+} removal occurs below the calculated pH values, but it is 50% near these pH values.

From Fig. 3 it can be seen that at pH 8 (Fig. A, Curve 1) about 80% flotation removal is achieved, and from Fig. 3(B) it is seen that virtually all of the feed cadmium is present in the solution as cadmium cations. A similar behavior can be observed for the other curves in this figure. From this it appears that the flotation process takes place at a smaller pH value than that of hydroxide precipitation. Such a situation results from the equation as well as from the solubility diagram of cadmium hydroxide as a pH function of the solution. Similar results have been obtained by Jurkiewicz (*18*) for zinc. This is probably due to the presence of the collector and ~1% alcohol in the solution, which may cause an earlier precipitation of the hydroxide. However, these factors are not considered either in calculations of the pH of hydroxide precipitation or in the solubility diagrams of various forms of cadmium. It may also be caused by the fact that lauryl sulfate anions can bind the $CdOH^+$ cations present in the solution before hydroxide precipitation. Therefore, the pH range in which the amount of metal in the hydroxide form increases coincides with the pH range of increasing cadmium removal. From Figs. 1 and 3 it may be concluded that the flotation curves and the hydroxide precipitation vs pH curves are parallel. Therefore, by knowing the isotherm of hydroxide precipitation, the flotation effectiveness relative to the pH of the solution can be predicted. Similar conclusions can be drawn from the studies of Bhattacharyya et al. (*6*) and others (*2–4, 9*).

Therefore, it may be assumed that a decrease of cadmium removal from ammonia media at a pH above 11 results from a decrease in the amount of hydroxide precipitate. This happens because $Cd(OH)_2$, which is practically insoluble in the presence of excess OH^- ions and NH_4^+, dissolves and forms complex ammonates of the type $(Cd(NH_3)_4)^{2+}$. In relation to these conditions, complex cations containing from 1 to 6 NH_3 molecules may occur (*21*). Analogous conclusions were drawn in the papers concerning cobalt, nickel, and copper (*15–17*).

From Fig. 2 it appears that the curve of flotation with lauryl sulfate is shifted in the direction of lower pH values in relation to that with Tween 80. This may be caused by the fact that negatively charged lauryl sulfate ions, apart from their hydrophobization of hydroxide sediment, may additionally bind Cd^{2+} and $CdOH^+$ cations present in equilibrium with the precipitate, while Tween 80, as a nonionic substance, only hydrophobizes the precipitate.

By analyzing the effect of electrolyte on the precipitate flotation of

cadmium hydroxide with lauryl sulfate, it was found that the efficiency of hydroxide removal decreases with an increase in the electrolyte concentration (Fig. 4, Curve 2). The adsorbing colloid flotation of Cd^{2+} changes as does that for hydroxide (Fig. 4, Curve 3). A similar influence of the electrolyte on the precipitate flotation of hydroxides of different metals is found in the works of Rubin and Lapp (*3, 4*), Sanak (*22*), and Jurkiewicz and Waksmundzki (*15–18*). Wilson et al. (*10–14*) have also published work dealing with the influence of electrolytes on adsorbing colloid flotation of metal cations.

Because specific adsorption of metal ions present in a solution at equilibrium with the precipitate takes place on hydroxide sediment, precipitate flotation shows the features of adsorbing colloid flotation. In this connection it is implied that in both cases the mechanism of hydrophobization of the precipitate by the collector is similar. Besides, the effectiveness of precipitate flotation of cadmium hydroxide and adsorbing colloid flotation of cadmium cations is similar to that of foam fractionation of cadmium cations from solutions of the electrolyte, as described earlier (*1*). Thus the mechanism of hydrophobization of hydroxide sediment can be elucidated on the basis of the reaction of the collector anions RSO_4^- with the positive surface ions formed due to adsorption or dissociation of surface groups (*23, 24*). In an earlier paper it was found that Na^+ ions compete with cadmium cations in relation to RSO_4^- anions (*1*). With an increasing concentration of sodium cations the reaction equilibrium shifts more and more in favor of the formation of hydrated ion pairs $(RSO_4^-,Na^+)_{(H_2O)_n}$. As a result, a larger and larger amount of lauryl sulfate undergoes adsorption on gas bubbles and enters the foam, and the hydroxide sediment remains in the bulk of the water phase. Because the collector and sodium cations are present in the solution, the above considerations clarify the participation of electrolyte cations in single flotation events occurring in the solution volume phase and at the gas bubble–liquid interface.

However, this does not clarify the participation of SO_4^{2-} anions in the flotation process. It can be assumed that positive sediment surface groups (*23, 24*), which could bind lauryl sulfate anions, are neutralized by sulfate anions due to preferential adsorption of these ions on the sediment, with an increase of salt concentration. Such an interpretation is suggested in the results published by Wilson's group (*25*) and by Jurkiewicz (*18*), where it was shown that adsorption of alkyl sulfate on $Fe(OH)_3$, $Al(OH)_3$, and $Zn(OH)_2$ decreases as the electrolyte concentration and valency of the electrolyte anion increase. Moreover, Pushkarev and Trofimov (*26*) showed that changes in the adsorption of alkyl sulfate on $Al(OH)_3$ depend on the nature of the salt used for hydroxide precipitation. This explains the competitive adsorption of ions present in the solution. The same trend was

observed by Bhattacharyya et al. (*6*). Alkyl sulfate anions, however, undergo adsorption with sodium counterions on the gas bubble. The sediment does not undergo hydrophobization then, and therefore remains in solution. This allows us to conclude that the influence of electrolyte anions on hydroxide flotation is related to the sediment surface properties. The facts presented account for the electrostatic mechanism of precipitate hydrophobization by the anion collector. Such a mechanism is confirmed by the flotation results obtained with the surface-active nonionic substance Tween 80, because the presence of electrolyte does not have an effect on hydroxide removal with this substance. On the basis of this fact, however, the mechanism of flotation by means of a nonionic collector cannot be specified.

The flotation mechanism is likely to differ in relation to the nature of the collector used. To elucidate this problem, further studies are needed to determine the value of collector adsorption on a hydroxide as well as the electric properties of the sediment surface in the flotation solution.

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