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Selective Removal of Cadmium from Mixed Metal Solution by Carbonate Infusion

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Abstract

The purpose of this study is to develop the technology of selective precipitation of a single metal from a mixed solution by carbonate infusion. Experiments were conducted in Pyrex reactors and jar testers. Synthetic wastewater of cadmium and copper mixed solution was used in this study. Initial cadmium and copper concentrations were 10^{-5}, 10^{-4}, and 10^{-3} *M*, which are the concentrations commonly occurring in electroplating rinsewater. The effects of pH, carbonate concentration, and mixing rate on copper and cadmium hydrolysis were investigated. The optimum conditions of selective precipitation for the cadmium form mixed solutions were around pH 9, and the mixing rate was 100 rpm.

INTRODUCTION

Many industrial wastewaters contain metals. These metals have potential economic value, and they are often strategic materials as well. Many are also toxic, and strict discharge limitations have been imposed by regulation. Several treatment technologies are available to achieve these discharge limitations. Of the various treatment methods employed to remove heavy metals, the most common is hydroxide precipitation, which is achieved by bringing the wastewater to an alkaline pH with lime or caustic.

The technology, as with other methods, is essentially based upon the concentration/separation process. A solid phase is formed and then separated by physical means to yield a sludge. These sludges often contain mixtures of metals, are perceived to have no economic value, and often must be managed and disposed of at high cost. If the separation of a single metal from a mixed metal solution is possible, this separated metal can be

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reused in a metal plating bath. Further, the cost of disposing of these metal sludges will be greatly reduced.

Processes for the selective removal of metal ions from a mixed metal solution can be broadly divided into two general categories: 1) biological processes and 2) chemical processes.

Biological processes remove or recover metal by the use of the high binding properties of certain microorganism and by the use of an elution scheme. It has been reported that algal-bound gold and mercury can be selectively eluted by using mercaptoethanol (*1*). Many investigators have shown that bacteria fungi and algae play a major role in removing metal ions from water (*2–7*). Agricultural wastes and by-products, industrial waste biomasses, and natural substances have been used to decontaminate wastewaters that contain metal ions (*8*).

Chemical processes for the selective removal of metal change the solubility properties of metals in mixed solutions by the addition of chemicals. The role of chemicals in this process is to change the nature of metal ions so they can be separated out sequentially. Even though many investigators have reported the removal of a single metal from single metal solutions or mixed metal solutions (*9*, *10*), techniques for the selective removal of a single metal from a mixed metal solution are rare.

In order to develop selective precipitation technology, the selective precipitation of a single metal from a mixed metal solution was investigated in this research. A two-metal system—cadmium and copper mixed solution—was considered in this study.

The experimentation was performed by using the hydroxide carbonate system because these two metals show reciprocal reactions with carbonate. The solubility of cadmium forms a "U" curve, and the solubility of copper forms a "W" curve (Fig. 1). These curves were developed by using the thermodynamic constants of cadmium and copper hydroxide species and the carbonate species of cadmium and copper. Constants were obtained from the literature (*11–14*).

Based on these solubility differences, cadmium precipitates out at its optimum point while copper exists as a soluble phase. We investigated copper and cadmium speciation in commonly occurring electroplating wastewater and the possible range of selective precipitation of a two-metal solution. By comparing the theoretical data, the viability of the selective recovery of cadmium from a mixed solution is discussed.

MATERIALS AND METHODS

Experiments were conducted to investigate the concentration change of soluble and precipitated copper and copper species at various conditions in a solution of known composition. The initial copper and cadmium con-

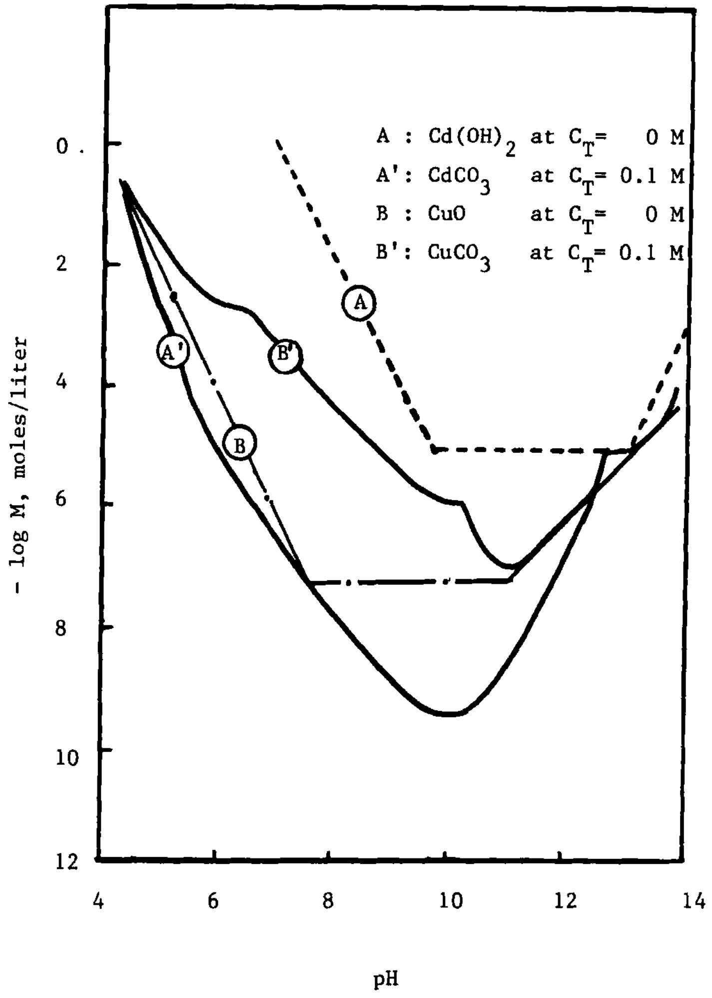

FIG. 1. Theoretical cadmium carbonate and copper carbonate solubility diagram.

centrations ranged from 10^{-5} to 10^{-3} *M*. This concentration range commonly occurs in electroplating rinsewater based upon the suggested formulation and make-up of copper and cadmium plating baths (*15*).

Table 1 shows the standard conditions of the experiment. The influence of possible constituents of electroplating wastewater was not considered in this study. All chemicals used were of analytical reagent grade. Stock cadmium or copper solution was prepared by dissolving cadmium nitrate or copper nitrate in distilled water, respectively. The pH was adjusted with

TABLE 1
Standard Conditions of Selective Precipitation

Total cadmium concentration	10^{-5}, 10^{-4}, 10^{-3} *M*
Total copper concentration	10^{-5}, 10^{-4}, 10^{-3} *M*
pH	8, 9, 10
Temperature	25°C
C_T	0, 0.1, 0.5 *M*
Ionic strength	$< 10^{-2.3}$ *M*
Sampling time (h)	0, 0.25, 0.5, 0.75, 1.0, 1.5, 3.0, 6.0, 12.0, 24.0, 36.0, 48.0

0.2 *N* HNO_3 or 0.2 *N* NaOH at a total carbonate concentration of 0 *M*. 10 *N* HNO_3 or 10 *N* NaOH was used to adjust the solution pH in the experiment of copper carbonate precipitation.

In order to achieve a total carbonate concentration of 10^{-1} or 0.5 *M*, sodium bicarbonate or sodium carbonate was used depending upon the specified pH. The calculated amount of sodium salts was weighed out and dissolved in distilled water. The solution was made up to volume and then infused with either carbon dioxide or nitrogen gas to raise or lower the desired pH, respectively. The amount of each chemical required was calculated by (*16*):

$$[\mathrm{Na^+}] = \frac{[\text{total carbonate}] \times (10^{-17.86} + 10^{-7.82}[\mathrm{H^+}])}{10^{-18.15} + 10^{-7.82}[\mathrm{H^+}] + 10^{-1.47}[\mathrm{H^+}]^2} - \frac{[\mathrm{H^+}]^2 - 10^{-14.0}}{[\mathrm{H^+}]} \qquad (1)$$

Equation (2) was used to determine the relationship between pH and total carbonate (C_T):

$$P_{\mathrm{CO_2}} = \frac{[\text{total carbonate}] \times [\mathrm{H^+}]^2}{10^{-18.15} + 10^{-7.82}[\mathrm{H^+}] + 10^{-1.47}[\mathrm{H^+}]^2} \qquad (2)$$

Carbonate concentrations were maintained constant (~0.1 *M*) during the entire experimental period.

All runs were conducted in a closed reactor at 25°C. The total volume of an experimental solution was 2 L. At predetermined time intervals, 50 mL aliquots were taken out and directly transferred to the filtration funnel. The portion retained on the filter was acidified with dilute nitric acid (0.2

N) and stored in prewashed polyethylene bottles. The filtrate was acidified with nitric acid (to the concentration of 0.2 *N*) and stored in prewashed polyethylene bottles. Metal analysis was performed by atomic absorption spectrophotometry using the open flame technique (Perkin-Elmer Model 2380B). Figure 2 shows a schematic diagram of the experimental apparatus.

The recovery loss of copper or cadmium was also determined. It was found that the recovery loss was due to adhesion of the precipitated copper or cadmium to the reactor wall. Based on this result, the unrecovered portion of cadmium or copper was considered to be the solid portion.

To test the effect of the mixing rates, experiments were performed by using a jar tester. The precipitability of cadmium and copper was investigated at mixing rates of 15, 50, 100, and 150 rpm. 50 mL aliquots were taken out every 12 h and filtered to separate the soluble and solid portions. The same methods as those of the main experiment were used for the acidification and analysis of each sample. The lowest concentration of precipitated copper was obtained at 100 to 150 rpm. The highest concentration of precipitated cadmium was obtained at 100 rpm. From those results, the optimum mixing rate for selective precipitation was determined to be 100 rpm.

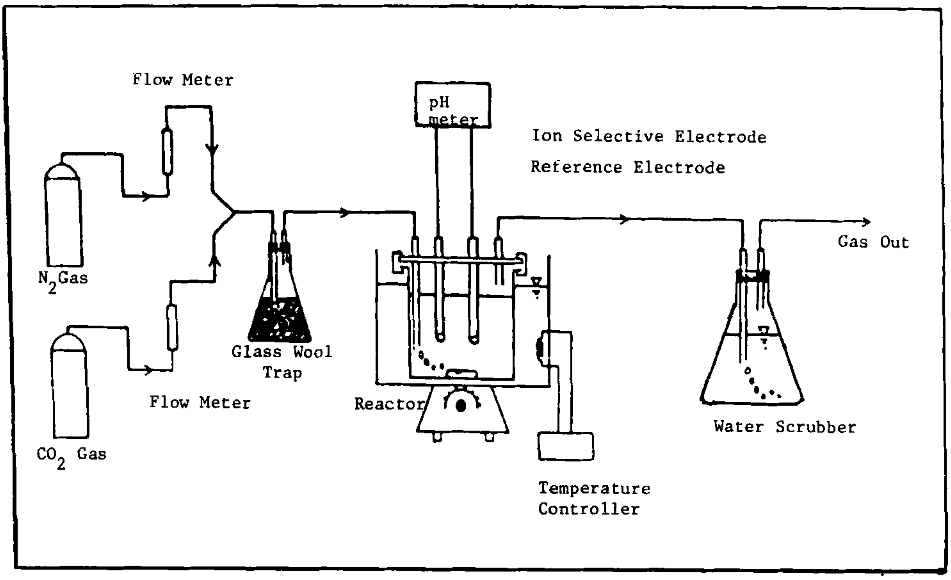

FIG. 2. Schematic diagram of experimental apparatus.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on copper hydrolysis was determined for samples with total carbonate concentrations of 0 and 10^{-1} *M*. The pH values were 8, 9, and 10. At a total copper concentration of 10^{-3} *M* and at $C_T = 0$ *M*, the final stable copper concentration (both soluble and precipitated portions) was close to the theoretical equilibrium concentration at all pH conditions (Fig. 3).

Similar trends were observed in the case of total copper concentrations of 10^{-4} and 10^{-5} *M*. At a total carbonate concentration of 10^{-1} *M*, the solubility of copper changed as theoretically predicted.

Maximum solubility of copper was observed at pH 9. It was also observed that the solubility of copper decreased with increasing total copper concentration. From these results it can be concluded that the optimum con-

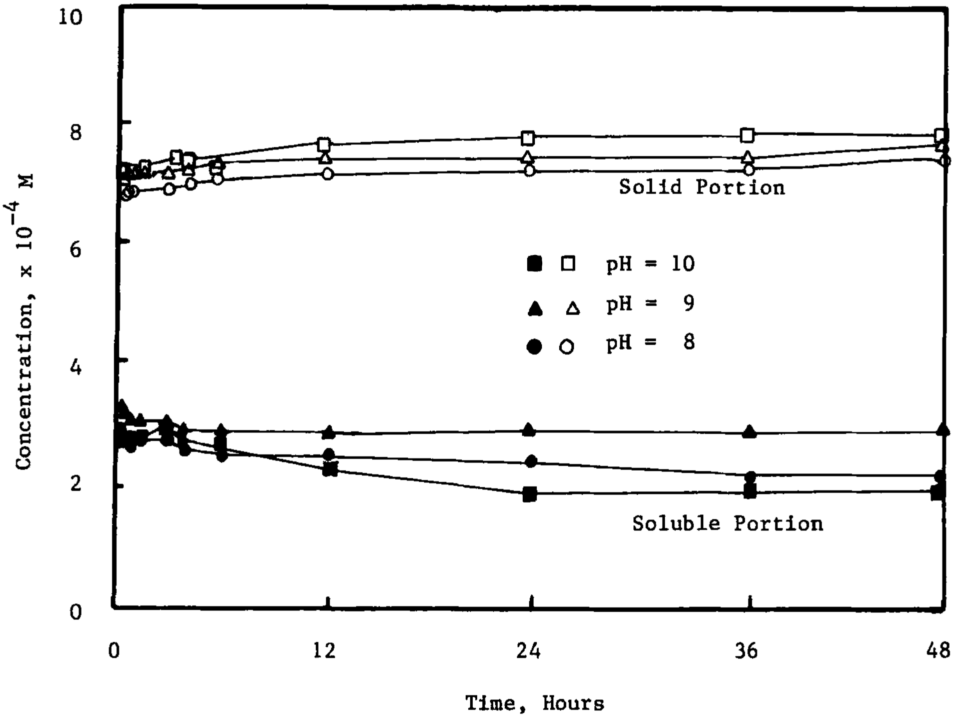

FIG. 3. Concentration of soluble and precipitated copper at various times ($Cu_T = 10^{-3}$ *M*, $C_T = 0$ *M*).

dition for selective precipitation would be around pH 9 and at a low rather than a high copper concentration.

Effects of Carbonate

Carbonate is another important controlling parameter of selective precipitation. In this research the solubility changes of copper and cadmium were investigated. Equilibrium was achieved with 6 h for both metals. The equilibrium concentration was obtained with these results by averaging the concentrations at 6, 12, 24, 36, and 48 h for each metal. Figure 4 shows the equilibrium concentrations of soluble copper at $C_T = 0$ and 10^{-1} M, and various pH values. Figure 5 shows the equilibrium concentration of soluble cadmium at $C_T = 0$ and 10^{-1} M, and various pH values. From these data it can be seen that the solubility of copper increased at pH 9

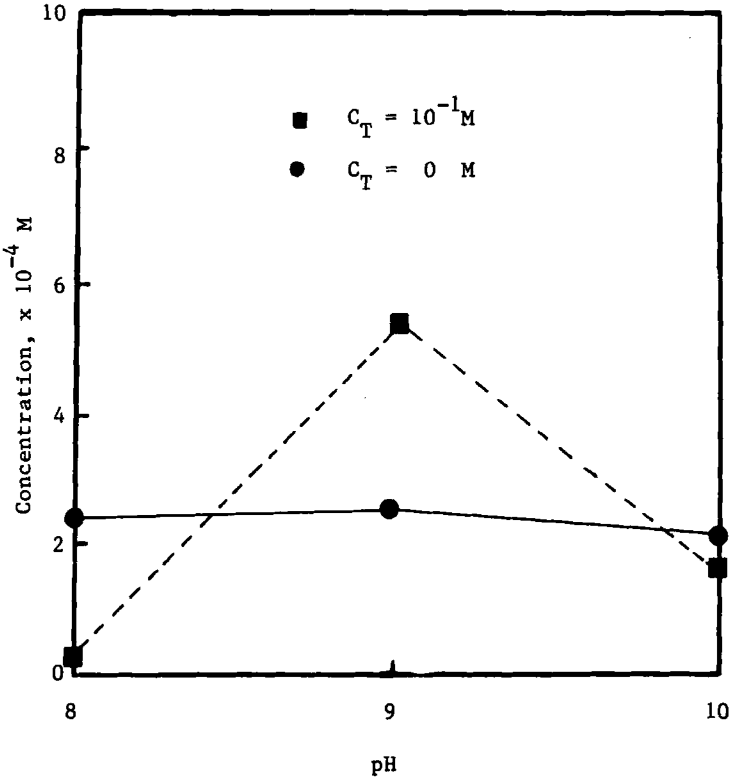

FIG. 4. Equilibrium soluble copper concentration at various pH values ($Cu_T = 10^{-3}$ M).

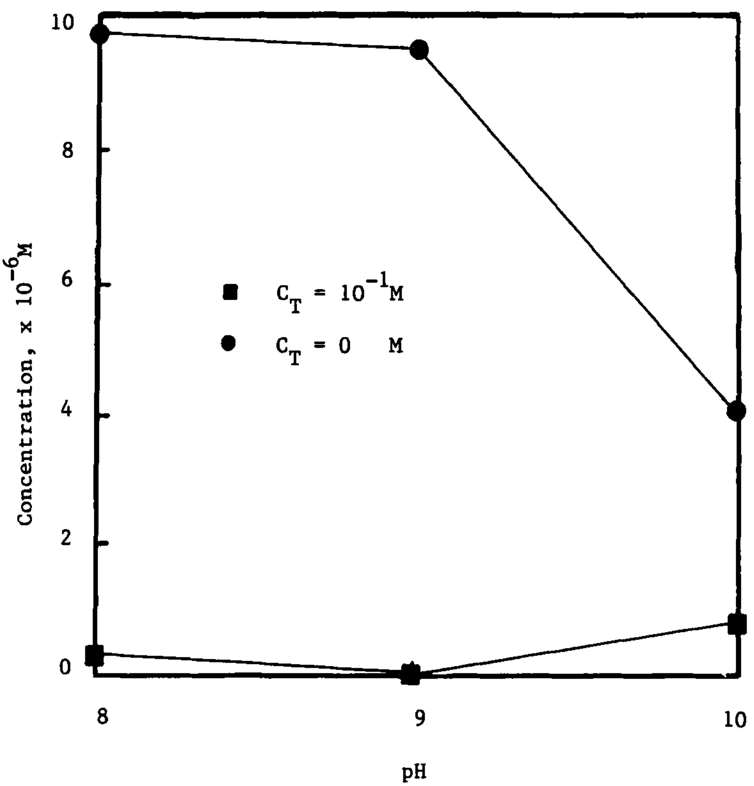

FIG. 5. Equilibrium soluble cadmium concentration at various pH values (Cd_T = 10^{-5} *M*).

by infusing the carbonate species. The solubility of cadmium decreased in the overall experimental pH range by infusing the carbonate species.

From these results it was concluded that the solubility of cadmium was decreased at all experimental pH conditions while the solubility of copper was increased at pH 9.

Selective Precipitation

Based on the results of our cadmium and copper precipitation study, experiments were performed to obtain the optimum conditions for selective precipitation by using the jar tester. Experimental conditions were Cu_T = 10^{-3}, 10^{-4}, or 10^{-5} *M*; Cd_T = 10^{-3}, 10^{-4}, or 10^{-5} *M*; C_T = 0.1 and 0.5 *M*; a mixing rate of 100 rpm; and pH 9. The pH was measured every 12 h during the experimental period. Even though it was observed that equilibrium was achieved within 6 h, the equilibration time was set at 24 or 48 h to assure complete equilibrium.

Table 2 shows the measured equilibrium concentration distribution of cadmium and copper species at pH 9 and $C_T = 10^{-1}$ *M*.

Comparison of these soluble and solid metal species with those predicted by MINEQL (*17*) showed that the measured distribution of each species has a pattern similar to those predicted by the theoretical MINEQL except for the condition $Cd_T = 10^{-3}$ *M*.

At $C_T = 0.1$ *M* and pH 9, the precipitated copper concentration increased with an increase of total copper concentration. At these conditions, 94 to 100% of the cadmium exists in the solid phase irrespective of the copper concentration (Fig. 6). The distribution of solid copper ranged from 22 to 86%, which indicates that there is little possibility of selective precipitation at these conditions.

At $C_T = 0.1$ *M*, pH 10, and $Cu_T = 10^{-3}$ *M* (Table 3, Fig. 7), over 89% of copper and over 99% of cadmium exist as solid phases. This also indicates the poor possibility of selective precipitation. The solubility of copper at pH 9 was higher than that at pH 10. This confirms that the optimum pH condition for selective precipitation of cadmium from copper is around pH 9.

By increasing the carbonate concentration to 0.5 *M*, the possibility of

TABLE 2
Distribution of Cadmium and Copper Species at pH 9, $C_T = 10^{-1}$ *M*

Conditions (*M*)	Metal species	*t* = 24 h Soluble portion (%)	Solid portion (%)
$Cu_T = 10^{-3}$	Cu	13.8	86.2
$Cd_T = 10^{-3}$	Cd	6.4	93.6
$Cu_T = 10^{-5}$	Cu	77.1	22.9
$Cd_T = 10^{-4}$	Cd	1.2	98.8
$Cu_T = 10^{-3}$	Cu	78.4	21.6
$Cd_T = 10^{-5}$	Cd	3.6	96.4
$Cu_T = 10^{-4}$	Cu	85.7	14.3
$Cd_T = 10^{-5}$	Cd	1.0	99.0
$Cu_T = 10^{-4}$	Cu	86.7	13.3
$Cd_T = 10^{-5}$	Cd	2.8	97.2
$Cu_T = 10^{-4}$	Cu	98.1	1.9
$Cd_T = 10^{-5}$	Cd	0	100

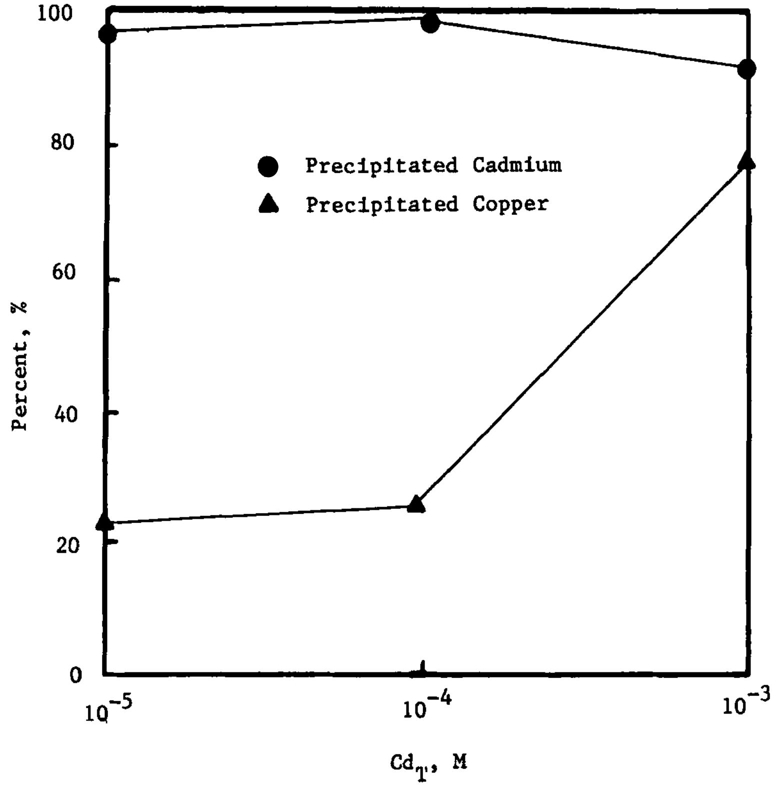

FIG. 6. Percent distribution of the solid portion of each metal at different cadmium concentrations ($Cu_T = 10^{-3}$ *M*, $C_T = 0.1$ *M*, pH 9).

TABLE 3
Distribution of Cadmium and Copper Species at pH 10, $C_T = 10^{-1}$ *M*

		t = 0 h		*t* = 24 h	
Conditions (*M*)	Metal species	Soluble portion (%)	Solid portion (%)	Soluble portion (%)	Solid portion (%)
$Cu_T = 10^{-3}$	Cu	22.5	77.5	10.9	89.1
$Cd_T = 10^{-3}$	Cd	4.7	95.3	1.1	98.9
$Cu_T = 10^{-3}$	Cu	29.4	70.6	10.6	89.4
$Cd_T = 10^{-4}$	Cd	3.9	96.1	1.0	99.0
$Cu_T = 10^{-3}$	Cu	20.1	79.9	10.3	89.7
$Cd_T = 10^{-5}$	Cd	15.4	84.6	0	100

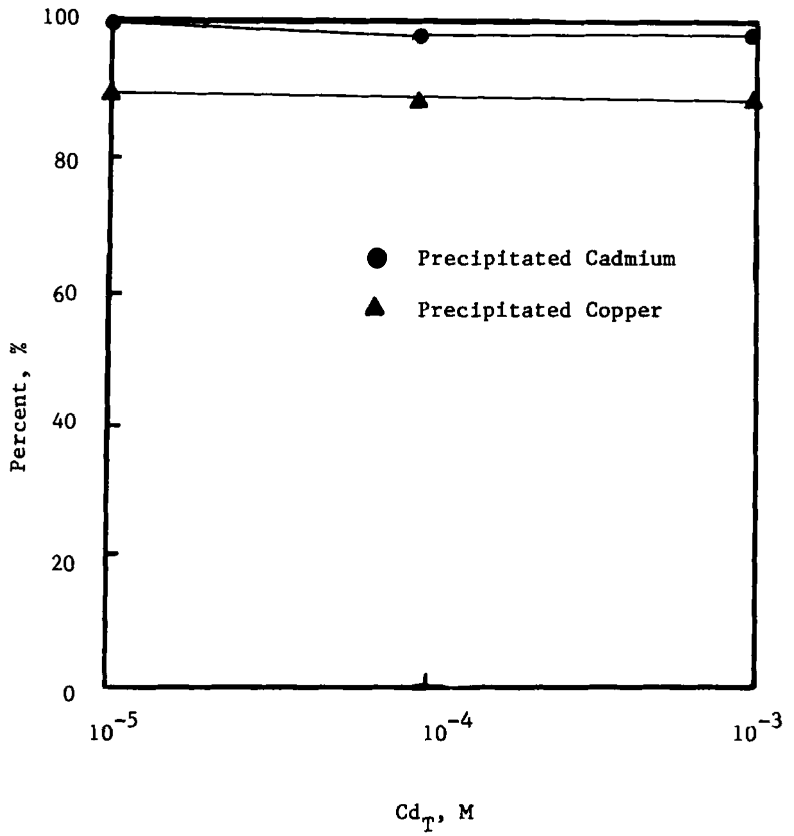

FIG. 7. Percent distribution of the solid portion of each metal at different cadmium concentrations ($Cu_T = 10^{-3}$ *M*, $C_T = 0.1$ *M*, pH 10).

selective precipitation increased. Table 4 shows the concentrations of cadmium and copper species at $C_T = 0.5$ *M*, pH 9 or 10, specified metal concentrations ($Cu_T = 10^{-3}$ *M*, $Cd_T = 10^{-3}$ *M*; $Cu_T = 10^{-4}$ *M*, $Cd_T = 10^{-4}$ *M*), and mixing rate of 30 or 100 rpm. At this high carbonate concentration, a large portion of copper exists as a soluble species. In general, a better possibility for selective recovery from a low copper concentration was obtained at a high mixing rate than at a low mixing rate.

Table 5 compares these measured soluble and solid metal distributions with those predicted by MINEQL. The measured distribution of each metal species showed a distribution similar to those predicted by the theoretical MINEQL. Among our experimental conditions, the most effective conditions for selective precipitation were $Cu_T = 10^{-4}$ *M*, $Cd_T = 10^{-4}$ *M*, and pH 9.

TABLE 4
Distribution of Cadmium and Copper Species at $C_T = 0.5\ M$

			$t = 0$ h		$t = 24$ h	
Conditions (M)	Mixing rate (rpm)	Metal species	Soluble portion (%)	Solid portion (%)	Soluble portion (%)	Solid portion (%)
$Cd_T = 10^{-3}$	30	Cu	90.8	9.2	82.9	17.1
$Cu_T = 10^{-3}$		Cd	8.2	91.8	1.7	98.3
pH 9	100	Cu	95.1	4.9	92.0	8.0
		Cd	2.8	97.2	0.9	99.1
$Cu_T = 10^{-4}$	30	Cu	99.0	1.0	98.8	1.2
$Cd_T = 10^{-4}$		Cd	4.1	95.9	1.3	98.7
pH 9	100	Cu	96.5	3.5	97.7	2.3
		Cd	4.1	95.9	1.3	98.7
$Cu_T = 10^{-3}$	30	Cu	90.5	9.5	91.1	8.9
$Cd_T = 10^{-3}$		Cd	3.9	96.1	1.0	99.0
pH 10						

TABLE 5
Comparison of Predicted and Experimental Results for Selective Precipitation at Various Conditions

			MINEQL prediction		Measured results	
Conditions (M)		Metal species	Soluble portion (%)	Solid portion (%)	Soluble portion (%)	Solid portion (%)
$C_T = 0.1$	$Cu_T = 10^{-3}$	Cu	11.5	88.3	10.9	89.1
	$Cd_T = 10^{-3}$	Cd	0	100	1.1	98.9
	pH 10					
	$Cu_T = 10^{-3}$	Cu	11.8	88.0	10.6	89.4
	$Cd_T = 10^{-4}$	Cd	0	100	1.0	99.0
	pH 10					
	$Cu_T = 10^{-3}$	Cu	11.8	88.0	10.3	89.7
	$Cd_T = 10^{-5}$	Cd	0	99.8	0	100
	pH 10					
$C_T = 0.5$	$Cu_T = 10^{-3}$	Cu	99.4	0	92.0	8.0
	$Cd_T = 10^{-5}$	Cd	0	100	0.9	99.1
	pH 9					
	$Cu_T = 10^{-4}$	Cu	99.4	0	97.7	2.3
	$Cd_T = 10^{-4}$	Cd	0	100	1.3	98.7
	pH 9					
	$Cu_T = 10^{-3}$	Cu	99.8	0	91.1	8.9
	$Cd_T = 10^{-3}$	Cd	0	100	1.0	99.0
	pH 10					

CONCLUSION

A comparison of copper carbonate precipitation with copper hydroxide clearly shows the expected increase in solubility due to copper carbonate compounds. The optimum conditions for selective precipitation obtained from this study are pH 9, $Cd_T = 10^{-4}\ M$, $Cu_T = 10^{-4}\ M$, and a high carbonate concentration.

In the case of cadmium and copper mixed solution, the selective removal of cadmium is a possible technique at the commonly occurring concentration of electroplating rinsewater. The controlling parameters for efficient selective precipitation can be summarized as high carbonate concentration, pH around 9, and optimum mixing rate of 100 rpm.

Acknowledgment

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