Coprecipitation of Cu(II) & Ni(II) Complexes with $Fe(OH)_3$

By Ona Gylienė, Mudis Šalkauskas and Neringa Vilčinskaitė

Metal complexes are widely used in the metal finishing industry. The presence of complexing agents, however, hinders metal recovery from waste effluents, particularly in the form of insoluble compounds. It has been shown recently that citrate and tartrate complexes of such metals as Zn(II), Ni(II), Co(II), and Pb(II) can be nearly completely coprecipitated at pH 10–12 as the hydroxides.[1] The extreme abundance of iron in the metal finishing industry implies the possibility of using $Fe(OH)_3$ instead of more valuable and (possibly) hazardous metals.

Much research has gone into $Fe(OH)_3$ coprecipitation with heavy metal cations. The formation of mixed precipitates, such as jarosites, occurs by hydroxide precipitation of mixed metals from sulfuric acid solutions in a mildly acid pH range: 3 to 6. The freshly precipitated $Fe(OH)_3$ forms ferrites with soluble metal cations, such as Cd(II), Cu(II), Ni(II), and Zn(II). Coprecipitation of ferrous and ferric cations to form ferrites with low concentrations of Ni(II) and Co(II) in citrate-containing solutions has been applied to removal of contaminants from rinsewater of electroless plating solutions.[2] C. Brooks[3] examined selective hydroxide precipita-

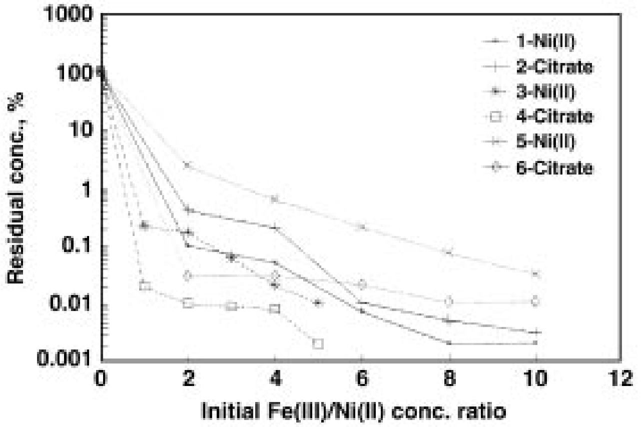

Fig. 1—Dependence of residual Ni(II) (1, 3, 5) and citrate (2, 4, 6) concentrations on initial Fe(III)/Ni(II) concentration ratio. Initial concentrations, mmol/L: 1, 2 - Ni(II), 50 - citrate, 20; 3, 4 Ni(II), 100 - citrate, 40; 5, 6 - Ni(II), 50 - citrate, 40.

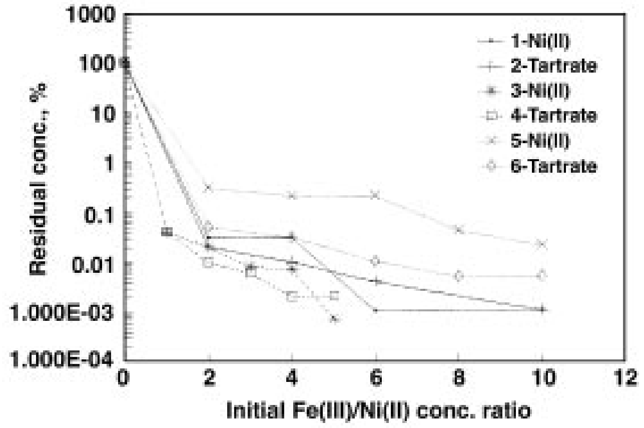

Fig. 2—Dependence of residual Ni(II) (1, 3, 5) and tartrate (2, 4, 6) concentrations on initial Fe(III)/Ni(II) concentration ratio. Initial concentration, mmol/L: 1, 2 - Ni(II), 50, tartrate, 20; 3, 4 Ni(II), 50 -tartrate, 40; 5, 6 - Ni(II), 100 - tartrate, 40.

Table 1
Precipitation of Ni(II)-Citrate Complexes by Fe(III)
pH 10

Initial conc., mmol/L			Residual conc., µmol/L	
Ni(II)	Citrate	Fe(III)	Ni(II)	Citrate
100	40	0	100,000	40,000
		100	220	6.9
		200	170	4.6
		300	70	3.4
		400	20	2.5
		500	15	1.6
50	40	0	50,000	40,000
		100	1300	13
		200	320	12
		300	100	7.6
		400	40	4.9
		500	20	4.1
50	20	0	50,000	20,000
		100	50	5.1
		200	30	2
		300	0.7	1.9
		400	0.3	0.9
		500	0.3	0.6

Table 2
Precipitation of Ni(II)-Tartrate Complexes by Fe(III)
pH 10

Initial conc., mmol/L			Residual conc., µmol/L	
Ni(II)	Tartrate	Fe(III)	Ni(II)	Tartrate
100	40	0	100,000	40,000
		100	45	15
		200	25	5.4
		300	8.5	2.6
		400	7.6	1
		500	0.7	0.8
50	40	0	50,000	40,000
		100	170	20
		200	110	10
		300	100	5
		400	20	3
		500	10	2
50	20	0	50,000	20,000
		100	15	5
		200	15	2
		300	0.4	0.8
		400	0.4	0.5
		500	0.4	0.3

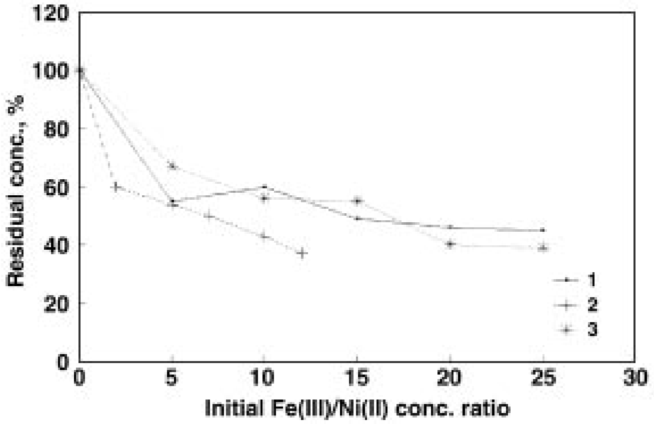

Fig. 3—Dependence of residual Ni(II) (1, 3, 5) on initial Fe(III)/Ni(II) concentration ratio. Initial concentrations, mmol/L: 1, 2 - Ni(II), 20 - EDTA, 40; 3, 4 - Ni(II), 40 - EDTA, 40; 5, 6 - Ni(II), 40 - EDTA, 20.

tion of Cu(II), Ni(II) and Fe(III) in a pH range of 3.5 to 4.5 from complexing-agent-containing solutions. The influence of the component addition sequence on nickel adsorption to $Fe(OH)_3$ in the presence of EDTA was studied by A.L Bryce *et al.*[4] When the Ni-EDTA complex was allowed to form prior to contact with $Fe(OH)_3$, nickel adsorption was observed at pH < 6, but was suppressed at pH > 7.

This paper examines $Fe(OH)_3$ coprecipitation with Ni(II) and Cu(II) complexes, such as citrate, tartrate, EDTA and glycine (aminoacetic acid), that are used for electroless nickel and copper plating. The present investigation is different from any of the studies cited above. Coprecipitation was carried out in the pH range of 8–10, where Ni(II) and Cu(II), as well as Fe(III), form stable complexes. In addition, the pH range is equivalent to that used in practice for metal recovery from wastewater and the concentration of metal complexes is similar to concentrations in wastewater after disposal of spent electroless plating solutions.

Table 3
Precipitation of Ni(II)-EDTA Complexes by Fe(III)
pH 10

Initial conc., mmol/L			Residual conc., µmol/L	
Ni(II)	EDTA	Fe(III)	Ni(II)	EDTA
40	40	0	40	0
		100	24	9
		200	22	0.2
		300	20	0.3
		400	17	0.4
		500	15	0.1
40	20	0	20	0
		100	14	7.5
		200	11	0.5
		300	11	0.2
		400	8	0.07
		500	8	0.04
20	40	0	20	0
		100	11	30
		200	12	14
		300	9.7	9.8
		400	9.2	7.1
		500	9	2.2

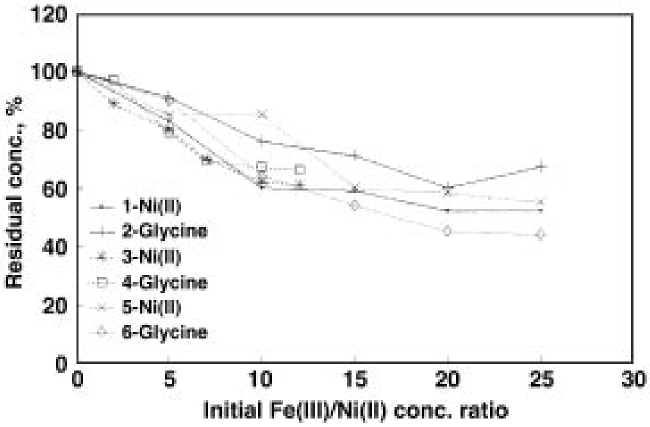

Fig. 4—Dependence of residual Ni(II) (1, 3, 5) and glycine (2, 4, 6) concentrations on initial Fe(III)/Ni(II) concentration ratio. Initial concentrations, mmol/L: 1, 2 - Ni(II), 20 - glycine, 150; 3, 4 - Ni(II), 40 - glycine, 150; 5, 6 - Ni(II), 40 - glycine, 80.

Experimental Procedure

Coprecipitation of metal complexes with $Fe(OH)_3$ was investigated by addition of $FeCl_3$ to metal complexes and adjusting the pH to 8–10 with NaOH. After about 24 hr, the precipitates were separated by filtration and the concentrations of the metals and complexing agents were determined in the filtrate.

The Ni(II) and Fe(III) concentrations were analyzed by titration with EDTA; Cu(II) by means of iodide; small quantities of metals, photometrically. Citrate and tartrate were determined with permanganate; glycine by titration with $NiSO_4$.[5]

Results and Discussion

Theoretically, metal concentration in alkaline solutions is limited by the concentration of a complexing agent. The presence of metal hydroxides, formed by excess of metal concentration, does not affect the concentration of metal complexes in solution. Practically, these concentrations are

Table 4
Precipitation of Ni(II)-Glycine Complexes by Fe(III)
pH 10

Initial conc., mmol/L			Residual conc., µmol/L	
Ni(II)	Glycine	Fe(III)	Ni(II)	Glycine
40	80	0	22	80
		100	17	72
		200	17	51
		300	12	43
		400	12	39
		500	11	35
40	150	0	40	150
		100	35	146
		200	32	118
		300	28	104
		400	25	101
		500	25	98
20	150	0	20	150
		100	17	138
		200	12	113
		300	12	106
		400	10	91
		500	10	87

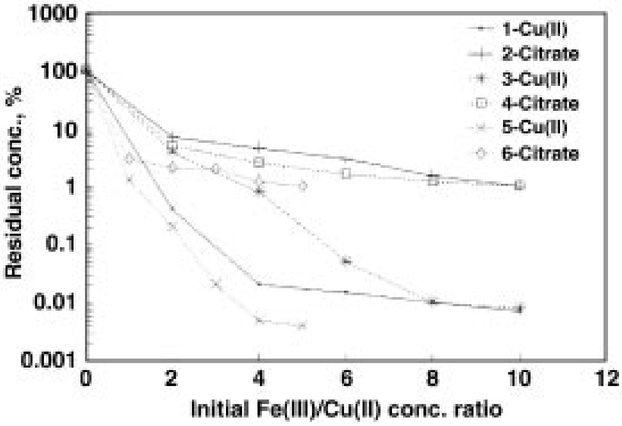

Fig. 5—Dependence of residual Cu(II) (1, 3, 5) and citrate (2, 4, 6) concentrations on initial Fe(III)/Cu(II) concentration ratio. Initial concentrations, mmol/L: 1, 2 - Cu(II), 50 - citrate, 20; 3, 4 - Cu(II), 50 - citrate, 40; 5, 6 - Cu(II), 100 - citrate, 40.

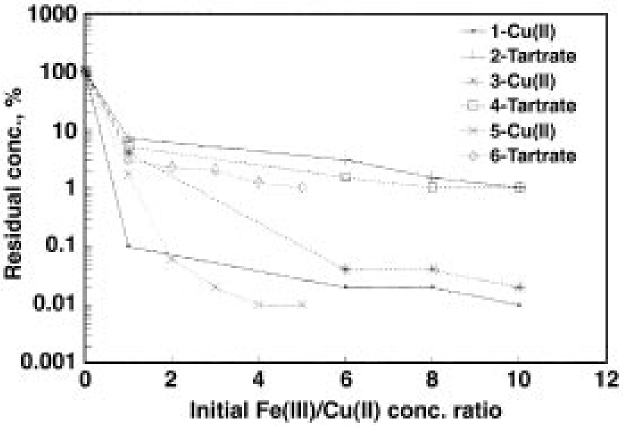

Fig. 6—Dependence of residual Cu(II) (1, 3, 5) and tartrate (2, 4, 6) concentrations on initial Fe(III)/Cu(II) concentration ratio. Initial concentrations, mmol/L: 1, 2 - Cu(II), 50 - tartrate, 20; 3, 4 - Cu(II), 50 - tartrate, 40; 5, 6 - Cu(II), 100 - tartrate, 40.

much less a result of the capability for sorption of freshly precipitated metal hydroxide. In some cases,[1] the decrease of metal complex concentration is so large that it cannot be explained by sorption of metal hydroxides.

To investigate the behavior of $Fe(OH)_3$ in metal complex solutions, the experiments were carried out with various concentrations of metal, complexing agents and Fe(III) (Tables 1–8). Listing of residual Ni(II), Cu(II) and complexing agent percentage vs. Fe(III)/Me(II) concentration shows the sharp dependence in citrate and tartrate solutions and slight dependence in EDTA and glycine solutions (Figs. 1–8).

The influence of pH is complicated—in the range of 8–10, pH does not affect the residual metal and complexing agent concentrations, but at pH 12, the decrease of residual concentrations in solution is inconsiderable (about 5–10 percent). At pH 12, Fe(III) does not form complexes, it precipitates as $Fe(OH)_3$. This partly explains the low coprecipitation of Ni-glycine and Cu-glycine complexes with $Fe(OH)_3$ (Figs. 4 and 8), to the extent that Fe(III) does not form complexes with glycine at any pH.

The precipitation of Ni-citrate (Fig. 1), Ni-tartrate (Fig. 2), Cu-citrate (Fig. 5) and Cu-tartrate (Fig. 6) complexes with $Fe(OH)_3$ is practically complete. It scarcely occurs from sorption of freshly precipitated $Fe(OH)_3$. The concentration of even 100 mM of Fe(III) (Table 1) precipitates 40 mM citrate and 100 mM Ni(II), while the limited metal complex concentration in solution can be 120 mM. It is probably responsible for the forming of insoluble compounds of Ni(II), Fe(III), citrate or tartrate and hydroxide.

Considerable amounts of Fe(III) remain in solution only at low (0.1–0.3 mol/L) initial Fe(III) concentrations (Table 3). At higher initial concentrations, the residual concentration is on the order of 10^{-6} to 10^{-7} mol/L. Only in the case of Ni-EDTA complexes is the residual Fe(III) concentration rather high. These data are in good agreement with results obtained by Bryce *et al.*[4] It is interesting to note that the differences

Table 5
Precipitation of Cu(II)-Citrate Complexes by Fe(III)
pH 10

Initial conc., mmol/L			Residual conc., µmol/L	
Cu(II)	**Citrate**	**Fe(III)**	**Cu(II)**	**Citrate**
100	40	0	100,000	40,000
		100	1300	1200
		200	190	900
		300	20	800
		400	5	500
		500	4	400
50	40	0	50,000	40,000
		100	2000	2000
		200	410	1000
		300	25	600
		400	5	500
		500	4	400
50	20	0	50,000	20,000
		100	200	1400
		200	10	900
		300	8	600
		400	5	300
		500	4	200

Table 6
Precipitation of Cu(II)-Tartrate Complexes by Fe(III)
pH 10

Initial conc., mmol/L			Residual conc., µmol/L	
Cu(II)	**Tartrate**	**Fe(III)**	**Cu(II)**	**Tartrate**
100	40	0	100,000	40,000
		100	1700	1200
		200	60	900
		300	24	800
		400	14	500
		500	13	400
50	40	0	50,000	40,000
		100	2000	2000
		200	740	1000
		300	20	600
		400	18	400
		500	10	400
50	20	0	50,000	20,000
		100	50	1400
		200	12	900
		300	9	600
		400	9	300
		500	8	200

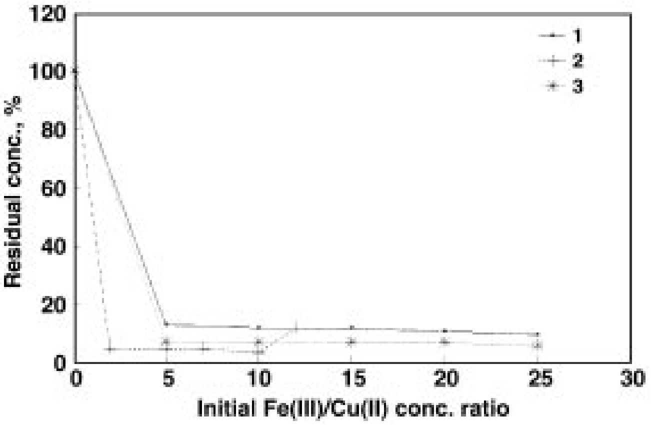

Fig. 7. Dependence of residual Cu(II) concentration on initial Fe(III)/ Cu(II) concentration ratio. Initial concentrations, mmol/L: 1 - Cu(II), 20 - EDTA, 40; 2 - Cu(II), 40 - EDTA, 40; 3 - Cu(II), 40 - EDTA, 20.

between coprecipitation of Ni(II) and Cu(II) complexes with $Fe(OH)_3$ are modest, except for EDTA complexes. The residual Cu(II) concentration is much less than that of Ni(II). The reason for this difference can be the ability of Cu(II) to form mixed EDTA-hydroxide complexes.

These studies indicate that coprecipitation with $Fe(OH)_3$ is very convenient for removal of Ni(II) and Cu(II) citrate and tartrate complexes and partly for Cu(II)-EDTA complexes. Coprecipitation with glycine complexes is low.

From separated precipitates, metal complexes can be recovered by addition of NaOH to pH 12 or more. Metal complexes are dissolved and $Fe(OH)_3$ remains as a precipitate with some Me(II) contamination.

Conclusions

1. Coprecipitation of Ni(II)-citrate, Ni(II)-tartrate, Cu(II)-citrate, and Cu(II)-tartrate complexes with $Fe(OH)_3$ is essentially complete and convenient for removal of these complexes from wastewater.

2. Coprecipitation with $Fe(OH)_3$ is not convenient for removal of Cu(II)-glycine, Ni(II)-glycine and Ni(II)-EDTA complexes.

Table 7
Precipitation of Cu(II)-EDTA Complexes by Fe(III)
pH 10

Initial conc., mmol/L			Residual conc., µmol/L
Cu(II)	EDTA	Fe(III)	Cu(II)
40	40	0	40
		100	2.1
		200	2.0
		300	2.0
		400	1.4
		500	1.4
40	20	0	20
		100	1.4
		200	1.4
		300	1.4
		400	1.4
		500	1.3
20	40	0	20
		100	2.6
		200	2.5
		300	2.5
		400	2.2
		500	2.1

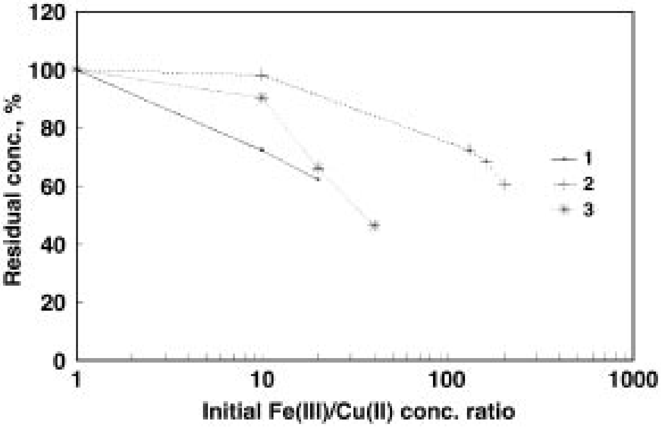

Fig. 8—Dependence of residual Cu(II) concentration on initial Fe(III)/ Cu(II) concentration ratio. Initial concentrations, mmol/L: 1- Cu(II), 20 - glycine, 80; 2 - Cu(II), 40 - glycine, 80; 3 - Cu(II), 40 - glycine, 40.

Editor's note: *Manuscript received, February 1996; revision received, July 1996.*

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Table 8
Precipitation of Cu(II)-Glycine Complexes by Fe(III)
pH 10

Initial conc., mmol/L			Residual conc., µmol/L
Cu(II)	Glycine	Fe(III)	Cu(II)
40	40	0	13
		100	13
		200	9.4
		300	8.3
		400	7.4
		500	6
40	80	0	25
		100	25
		200	24
		300	18
		400	17
		500	15
20	80	0	20
		100	15
		200	14
		300	13
		400	12
		500	10

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