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Recovery of Heavy Metals with Calcium Silicon Alloy. II. Recovery of Copper(II) Ions

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In the 20.0-matom dm^{-3} Cu(II) solution of an initial pH of 4.0, more than 99% of it was removed by addition of calcium silicon alloy in *ca.* 5 min, and the pH decreased to below 2. The X-ray diffraction pattern of the solid reaction product indicated that the Cu(II) removal took place through reduction to metallic Cu. In the 1.0-matom dm^{-3} Cu(II) solution, the pH increased from 4.0 to above 9.0 in 30 min, which consequently maintained high removal for a long time. In the constant pH runs, relation of the equivalents of Ca and Si dissolved against that of Cu(II) ions removed showed that not only the Ca moiety but also the Si moiety participated in the reduction of Cu(II) ions. It is desirable to control pH value at 3.0 or higher, or to separate the solid phase from the liquid phase in the first 30—60 min in order to avoid excess dissolution of calcium silicon alloy and to attain high Cu(II) removal. Copper(I) oxide was formed in a solution of pH above *ca.* 5, which was in contact with the air. In a HNO_3 solution, the removal decreased considerably. Sodium nitrate also caused strong interference with the removal which can be prevented by acidifying the solution with HCl to pH *ca.* 1. When Hg(II) or Cr(VI) ions are present, the Cu(II) removal tends to decrease depending on the amount of calcium silicon alloy added.

In the previous study,[1)] calcium silicon alloy proved to be effective for reducing metal ions such as Cd(II), Sn(II), Pb(II), Cu(II), Ag(I), and Hg(II) ions to the elemental state. Fe(III) and Cr(VI) ions were reduced to Fe(II) and Cr(III), respectively. The solubility of calcium silicon alloy is insignificant at pH 3—8, making its use as a reductant possible in aqueous solutions without causing excess dissolution. The reduction of Hg(II) ions with the alloy was studied in detail previously.[2)] The purpose of the present paper is to study in detail the recovery of copper(II) ions with calcium silicon alloy and to find the optimum conditions for recovering them in metallic powder which is more advantageous for further utilization than copper(I) compounds.

Experimental

Materials. The same calcium silicon alloy as used previously[1)] was used. All other chemicals were of reagent grade. As Cu(II) solution copper(II) chloride was used.

Analysis. Analyses of Cu, Cd, Pb, Fe, Hg, Cr, Ca, and Si were made as reported previously.[1)]

X-Ray Powder Diffraction. The X-ray powder diffraction pattern of a solid product was obtained with a Model 2025 Diffractometer (Rigaku Corporation) with Ni-filtered Cu *Kα* radiation. Quantitative determination of copper(I) oxide was carried out by preparing a calibration curve with standard mixtures of copper(I) oxide and copper metal powder, and with the diffraction peaks at 2.47 and 2.08 Å, respectively.

Recovery of Copper(II) Ions without pH Control. A 2.0 dm^3 of 20.0- or 1.0-matom dm^{-3} Cu(II) solution was prepared in a beaker and the pH was adjusted to 4.0 with HCl. The beaker was placed in a 20 °C thermostat, and its opening was covered with a film of polyethylene which had a short rift for addition of calcium silicon alloy and for sampling. Six grams of calcium silicon alloy was added, and the solution was stirred continuously with a magnetic stirrer. Then an aliquot was taken at intervals and filtered through a membrane filter (Millipore, WH) as quickly as possible. Analysis was made on the filtrate for Cu, Ca, and Si, and the pH was determined. Selected samples of the solid product obtained from the 20.0-matom dm^{-3} Cu(II) run were washed with a small amount of water and dried in a vacuum drying oven at *ca.* 60 °C for 2 d, and then analyzed by the X-ray powder diffraction method.

Recovery of Copper (II) Ions at Constant pH. To a 2.0 dm^3 of 30.0-, 20.0-, 10.0-, 5.0-, or 1.0-matom dm^{-3} Cu(II) solution was added 6.0 g of calcium silicon alloy. The pH was maintained constant at 4.0 by automatically adding either NaOH or HCl solution with a Model HSM-10A pH Stat (Toa Electronics Ltd.). Furthermore the pH of a 1.0-matom dm^{-3} Cu(II) solution was controlled at 6.0, 4.0, 3.0, or 2.0 with HCl. The same procedure was followed as above.

Air Oxidation of Metallic Copper. A 20.0-matom dm^{-3} Cu(II) solution of an initial pH of 4.0 was treated in the same way as above without covering the opening of the beaker with a polyethylene film.

Interferences on the Reduction of Copper(II) Ions. Interference from Acids. A 100 cm^3 of 1.0-matom dm^{-3} Cu(II) solution was prepared in a 100-cm^3 Erlenmeyer flask whose acidity was adjusted with HCl, HNO_3, H_2SO_4, or $HClO_4$ to pH *ca.* 3, *ca.* 1, and 1.0 mol dm^{-3} acid. To the solution was added 0.3 g of calcium silicon alloy and the opening of the flask was sealed with "Parafilm." The solution was stirred with a magnetic stirrer in a 20 °C thermostat, and filtered through a membrane filter 30 min after the addition of calcium silicon alloy. Determination was made for Cu, Ca, Si, and pH on the filtrate.

Interference from Sodium Salts. A 100 cm^3 of 1.0-matom dm^{-3} Cu(II) solution was prepared in a 100-cm^3 flask which contained NaCl, $NaNO_3$, Na_2SO_4, or $NaClO_4$ in the concentration of 0.1, 1.0, 10.0, or 100.0 mmol dm^{-3}. The pH was adjusted to *ca.* 3 with HCl. Then the sample solution was treated in the same way as above.

Interference from Metal Ions. A 100 cm^3 of 1.0-matom dm^{-3} Cu(II) solution was prepared, which contained $CdCl_2$, $PbCl_2$, $FeCl_3$, $HgCl_2$, or K_2CrO_4 in the concentration of 0.1, 1.0, 5.0, or 20.0 mmol dm^{-3}. The pH was adjusted to *ca.* 3 with HCl. As the reference, a 100 cm^3 of metal mixture solution was prepared containing 1.0 mmol dm^{-3} of $CuCl_2$ and each 1.0, 5.0, or 10.0 mmol dm^{-3} of $CdCl_2$, $PbCl_2$, $FeCl_3$, and $HgCl_2$. The sample solution was treated in the same way as above.

Results and Discussion

Recovery of Copper(II) Ions without pH Control.

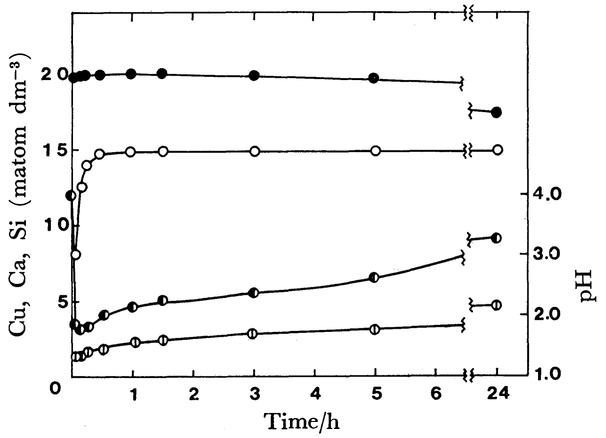

Fig. 1. Recovery of Cu(II) ions at an initial pH of 4.0. 20.0-matom dm^{-3} Cu(II) solution.
●: Cu(II) removed, matom dm^{-3}, ○: Ca dissolved, matom dm^{-3}, ⦶: Si dissolved, matom dm^{-3}, ◐: pH.

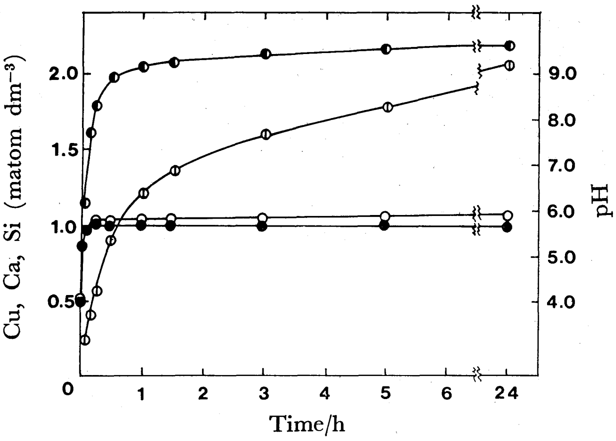

Fig. 2. Recovery of Cu(II) ions at an initial pH of 4.0. 1.0-matom dm^{-3} Cu(II) solution.
●: Cu(II) removed, matom dm^{-3}, ○: Ca dissolved, matom dm^{-3}, ⦶: Si dissolved, matom dm^{-3}, ◐: pH.

The efficiency of calcium silicon alloy for recovering Cu(II) ions was studied by determining removal rates of Cu(II) ions, dissolution rates of the Ca and Si moieties from the alloy, and the variation of pH, and by using the X-ray diffraction patterns of the obtained solid product. The pH of the Cu(II) solutions was initially adjusted to 4.0. The results are given in Figs. 1 and 2.

In the 20.0-matom dm^{-3} Cu(II) solution, the removal rate of Cu(II) ions was so great at the initial stage of the reaction that more than 99% removal was attained in *ca.* 5 min, the remaining Cu(II) concentration being lower than *ca.* 0.03 matom dm^{-3}. With the Cu(II) removal, the pH decreased remarkably from 4.0 to below 2.0, and then increased slowly. Such a great decrease in pH was observed for solutions of more concentrated than *ca.* 5-matom dm^{-3} Cu(II). The X-ray diffraction analysis showed that all of the solid products recovered on the membrane filter contained only metallic Cu as the copper component, indicating that Cu(II) ions were removed through reduction to metallic Cu. The dissolution of Ca and Si increased in accordance with the Cu(II) removal at the initial stage of the reaction, and thereafter the former reaction terminated in *ca.* 30 min, whereas the latter reaction continued to increase slowly with time. Although excess calcium silicon alloy was present in the solution, the Cu(II) concentration in the solution began to increase after *ca.* 3 h, indicating dissolution of deposited Cu again into solution. In this case, the amount of Ca dissolved was *ca.* 15 matom dm^{-3}, amounting to *ca.* 64% of the Ca moiety initially present. The Ca dissolution seems to take place from the surface of the alloy, the Ca moiety remaining just inside the alloy particles, and it was made inactive by being surrounded by silicates and the Si moiety. The reduction of Cu(II) ions by the Si moiety seems to be slower than the dissolution of metallic Cu.

In the 1.0-matom dm^{-3} Cu(II) solution (Fig. 2), the removal rate of Cu(II) ions was also great at the initial stage of the reaction, and the Cu(II) concentration was held below 0.001 matom dm^{-3}. The removal rate in percentage was slightly smaller than that for the 20.0-matom dm^{-3} Cu(II) solution. In contrast to the 20.0-matom dm^{-3} run, the pH increased considerably to above 9.0 in 30 min, which acted to depress dissolution of deposited metallic Cu, and consequently high Cu(II) removal was maintained for as long as 24 h. The amount of Ca dissolved increased with that of Cu(II) removed, their equivalents showing a good agreement. The increase in pH seems to depress excess Ca dissolution. On the other hand, the Si dissolution increased linearly independent of the Cu(II) removal, exceeding the dissolved Ca moles after *ca.* 40 min. It can be concluded that Cu(II) ions are removed by being reduced to the metal mainly with the Ca moiety.

Recovery of Copper(II) Ions at a Constant pH. The pH of the sample solution tends to vary considerably during the reaction, decreasing for Cu(II) concentrations higher than *ca.* 5 matom dm^{-3}, and increasing for lower Cu(II) concentrations. Similar experiments were carried out keeping the pH constant in order to study the reaction in detail without the effects of the pH variation.

Effects of initial Cu(II) concentrations on the reaction were studied with 30.0-, 20.0-, 10.0-, 5.0-, and 1.0-matom dm^{-3} Cu(II) solutions of pH 4.0, where the dissolution of the alloy is insignificant in a metal-free solution(blank).[1] Since the pH decreased at the initial stage of the reaction (*ca.* 5 min) for Cu(II) concentrations higher than 5 matom dm^{-3}, 1—4 mol dm^{-3} NaOH solution was added to control the pH. The results are given in Table 1 (Runs 1 to 5). In all the runs more than 99% removal was attained in as soon as 15 min, showing a very high removal efficiency. The removal rate (%) in the first 5 min was greater for higher initial Cu(II) concentrations. All the X-ray diffraction patterns of the solid products obtained from the 30.0—5.0-matom dm^{-3} runs showed that only metallic Cu was contained as the copper component. Thus, it can be concluded that the Cu(II) removal takes place through reduction to metallic Cu. Though the solid products obtained from the 1.0-matom dm^{-3} Cu(II) run failed to give X-ray diffraction pattern of copper compounds due to their

Table 1. Recovery of copper(ii) ions at constant pH

Run	Initial Cu(II) (matom dm^{-3})	pH		Time/min 5	15	30	60	90	180	300	420
1	30	4.0	Cu[a]	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
			Ca[b]	14.0	14.4	14.8	14.9	15.1	15.2	15.3	15.2
			Si[c]	2.0	2.2	2.3	2.6	2.9	3.1	3.3	3.6
2	20	4.0	Cu	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
			Ca	11.5	11.7	11.9	12.0	12.1	12.0	12.0	12.0
			Si	1.4	1.4	1.5	1.6	1.7	2.0	2.4	2.8
3	10	4.0	Cu	9.9	10.0	10.0	10.0	10.0	10.0	10.0	10.0
			Ca	6.6	6.7	6.9	7.2	7.5	8.2	8.8	9.1
			Si	0.6	0.7	0.8	0.9	1.1	1.4	1.9	2.1
4	5.0	4.0	Cu	4.6	5.0	5.0	5.0	5.0	5.0	5.0	5.0
			Ca	4.0	4.2	4.3	4.6	4.8	5.3	5.9	6.3
			Si	0.3	0.3	0.4	0.5	0.6	0.8	1.1	1.4
5	1.0	4.0	Cu	0.84	0.99	1.00	1.00	1.00	0.98	0.97	0.96
			Ca	0.89	1.09	1.12	1.53	1.83	2.54	3.22	3.86
			Si	0.04	0.10	0.16	0.21	0.27	0.45	0.63	0.82
6	1.0	6.0	Cu	0.74	0.98	1.00	1.00	1.00	1.00	0.99	0.98
			Ca	0.80	1.04	1.25	1.53	1.76	2.21	2.95	3.33
			Si	0.05	0.12	0.25	0.41	0.59	0.98	1.39	1.72
7	1.0	3.0	Cu	0.95	1.00	1.00	1.00	0.99	0.98	0.95	0.90
			Ca	1.07	1.23	1.34	1.63	1.95	2.75	3.72	4.56
			Si	0.07	0.12	0.18	0.26	0.33	0.57	0.92	1.37
8	1.0	2.0	Cu	0.98	1.00	1.00	1.00	0.95	0.65	0.15	0.04
			Ca	2.53	5.83	6.95	7.17	7.18	7.22	7.19	7.23
			Si	0.14	0.34	0.58	1.38	1.54	2.37	3.24	3.93

a) Cu(II) removal, matom dm^{-3}. b) Ca dissolution, matom dm^{-3}. c) Si dissolution, matom dm^{-3}.

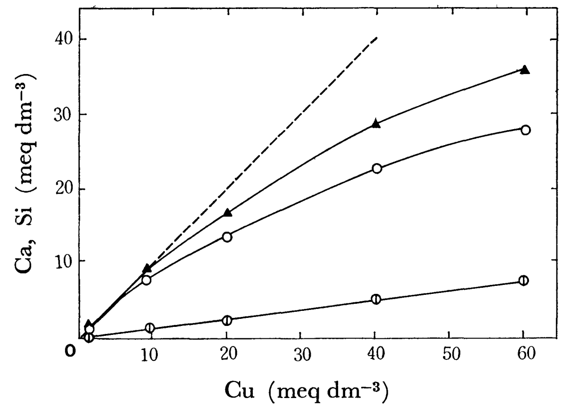

Fig. 3. Relation between equivalent of Cu(II) ions removed and those of Ca and Si dissolved.
○: Ca dissolved, meq dm^{-3}, ⦶: Si dissolved, meq dm^{-3}, ▲: Ca+Si dissolved, meq dm^{-3}.

low contents, metallic Cu seems to be present in them.

The dissolution of Ca and Si took place in accordance with the Cu(II) removal. In the 30.0- and 20.0-matom dm^{-3} solutions, the amount of Ca dissolved reached a plateau several min after the Cu(II) removal had completed, where greater part (*ca.* 50—60%) of the Ca moiety initially contained in the alloy dissolved. The Si dissolution amounted to, at most, less than 5% of the initial Si moiety, increasing linearly even after the completion of Cu(II) removal. For the stoichiometrical discussion, the equivalents of Ca and Si dissolved and their sum are plotted against that of Cu(II) ions removed (Fig. 3), where the values at 5 min after the alloy addition are used, since the Ca and Si dissolutions tend to increase even after the completion of Cu(II) removal. The Ca dissolution showed a relation not linear to the Cu(II) removal, but it is undoubtful that the Ca moiety mainly acted to reduce Cu(II) ions. The Si dissolution showed a direct proportionality to the Cu(II) removal, indicating that not only the Ca moiety but also the Si moiety participated in the reduction, but the extent of its participation was much smaller than that of the former. The ratios of the sum of the equivalents of Ca and Si dissolved to that of Cu(II) ions removed were close to unity at 1.0 and 5.0 matom dm^{-3}, well accounting for the Cu(II) removal. At higher Cu(II) concentrations, however, the ratios became smaller, the reason of which is not clear yet.

Then, the effects of pH on the reaction were studied with 1.0-matom dm^{-3} Cu(II) solutions whose pH was controlled at 6.0, 4.0, 3.0, and 2.0 (Table 1, Runs 5 to 8). The removal rate of Cu(II) ions at the initial stage of the reaction was appreciably greater at lower pH, showing that an acid condition favors the reduction of Cu(II) ions. But the dissolution of deposited metallic Cu became more significant in stronger acid solutions, the Cu(II) removal decreasing down to almost zero after 3 h at pH 2.0. Furthermore the

Table 2. Effects of acids on recovery of Cu(II) ions

Acid	Acidity[a) Initial	Acidity[a) Final	Cu(II) removal (%)	Ca diss. (matom dm^{-3})	Si diss. (matom dm^{-3})
HCl	4.1	9.0	99.9	1.4	0.4
	2.9	3.9	99.8	1.7	0.2
	2.0	3.5	99.9	6.0	0.7
	1.0	1.1	99.4	9.7	1.3
	[1.0]	—	97.5	10.4	1.5
HNO_3	3.1	3.3	16.8	0.4	0
	1.2	1.2	1.1	0.4	0
	[1.0]	—	2.1	0.7	0.1
H_2SO_4	3.0	3.7	99.8	1.0	0.2
	1.2	1.3	99.7	7.9	0.9
	[1.0]	—	99.8	8.5	1.3
$HClO_4$	3.0	3.7	99.8	1.0	0.2
	1.0	1.0	99.7	9.0	1.0
	[1.0]	—	99.7	9.7	1.4

a) Figures in parentheses are expressed in mol dm^{-3}, and others in pH unit.

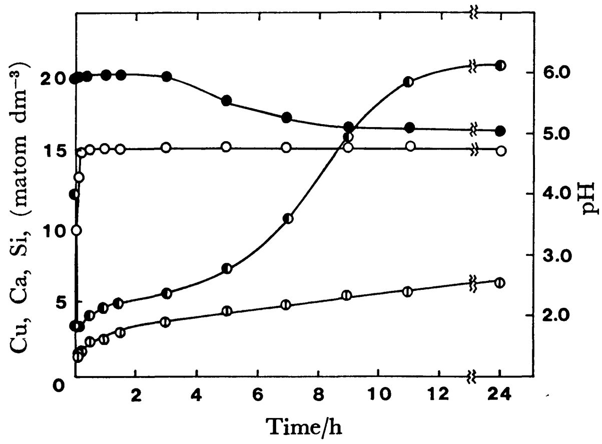

Fig. 4. Recovery of Cu(II) ions at an initial pH of 4.0 under the air. 20.0-matom dm^{-3} Cu(II) solution. ●: Cu(II) removed, matom dm^{-3}, ○: Ca dissolved, matom dm^{-3}, ⦶: Si dissolved, matom dm^{-3}, ◐: pH.

dissolution of Ca and Si was much greater in such a strong acid condition. In the pH 6.0—3.0 runs, the equivalents of Ca dissolution at the initial stage well accounted for that of Cu(II) removal, increasing linearly with time after the completion of Cu(II) removal. It is, therefore, desirable to control pH value at 3.0 or higher, or to separate the solid phase from the solution in the first 30—60 min in order to avoid excess dissolution of the alloy and to establish complete Cu(II) removal.

Air Oxidation of Metallic Copper. When a solid product containing metallic Cu had been dried, copper was stable to the air for a long time, but when a wet product was placed in the air, formation of copper(I) oxide was recognized by its X-ray diffraction pattern, its intensity becoming significant with time. This indicates that metallic Cu is subject to air oxidation under a wet condition. When the product had been dried under reduced pressure as quickly as possible, the oxidation did not take place. Thus the air oxidation can be avoided in this way. Then the conditions were examined to cause the air oxidation of metallic Cu by making a similar experiment in the air, *i.e.* without a polyethylene film in the opening of a beaker. The result is shown in Fig. 4, and compared with that of the above-mentioned run with the solution isolated from the air (Fig. 1). The Ca dissolution showed a similar tendency with that of the above run. On the other hand, the Si dissolution was slightly greater. More than 99% Cu(II) removal was maintained for *ca.* 3 h. Thereafter the Cu(II) concentration in the solution began to increase with an increase in pH. At that time the solid product contained only metallic Cu as the copper component, indicating the reaction $Cu+1/2\,O_2+H_2O=Cu^{2+}+2\,OH^-$. After *ca.* 9 h the pH rose above *ca.* 5, and the increase in the Cu(II) concentration ceased. Then formation of copper(I) oxide was recognized in the solid product, and its content increased with time, indicating progress of its air oxidation. After 24 h metallic Cu in the solid phase changed entirely into copper(I) oxide. In another run in the air at pH 4.0, no appreciable amount of copper(I) oxide was found, and high Cu(II) removal was held for a long time. Therefore, it is found that deposited metallic Cu is stable for *ca.* 3 h in the air, and that its air oxidation is made insignificant by separating the solid product from the solution in a short time even if the reaction is carried out in the air. Thus the air oxidation yields Cu(II) ions when the pH is below *ca.* 5, decreasing the Cu(II) removal, and yields copper(I) oxide at pH higher than 5.

Interferences on the Reduction of Copper(II) Ions. For the actual calcium silicon alloy process, effects of commonly used acids and salts on the reduction of Cu(II) ions were studied, and those of metal ions as well, which are reduced to the lower oxidation state with the alloy. The results obtained in 30 min after addition of the alloy were discussed, when the removal was complete and the dissolution of deposited

TABLE 3. EFFECTS OF SODIUM SALTS ON RECOVERY OF Cu(II) IONS

Sodium salt		pH		Cu(II) removal (%)	Ca diss. (matom dm^{-3})	Si diss. (matom dm^{-3})
	(mmol dm^{-3})	Initial	Final			
NaCl	0.1	3.1	3.8	98.9	1.1	0.2
	1.0	3.0	5.7	99.1	1.2	0.2
	10.0	3.0	6.4	99.1	1.1	0.2
	100.0	3.0	7.6	99.8	1.2	0.3
$NaNO_3$	0.1	3.0	3.2	90.1	0.9	0.2
	1.0	2.9	4.8	37.6	0.6	0.1
	10.0	3.0	3.9	5.9	0.2	0
	10.0	1.0	1.0	99.5	8.1	1.0
	100.0	3.0	3.9	3.9	0.2	0
	100.0	1.0	1.0	11.1	0.7	0.2
Na_2SO_4	0.1	3.0	4.4	99.9	1.0	0.1
	1.0	3.0	4.1	99.8	1.1	0.2
	10.0	3.1	3.7	83.1	1.1	0.2
	100.0	3.0	3.4	79.3	1.2	0.2
	100.0	1.0	1.0	99.6	7.6	1.3
$NaClO_4$	0.1	3.0	4.5	99.8	1.0	0.2
	1.0	3.0	4.0	99.5	1.0	0.2
	10.0	3.1	4.3	99.7	1.1	0.2
	100.0	3.0	5.4	99.9	1.4	0.3

TABLE 4. EFFECTS OF METAL IONS ON RECOVERY OF Cu(II) IONS

Metal salt		pH		Cu(II) removal (%)	Metal removal (%)	Ca diss. (matom dm^{-3})	Si diss. (matom dm^{-3})
	(mmol dm^{-3})	Initial	Final				
$CdCl_2$	0.1	3.0	3.7	99.6	0.8	1.0	0.2
	1.0	3.1	3.7	98.8	0.6	1.1	0.2
	3.0	2.9	3.7	98.7	8.2	1.2	0.2
	10.0	2.8	3.3	99.3	27.3	3.2	0.4
	20.0	3.0	2.1	99.0	16.6	3.8	0.5
$PbCl_2$	0.1	3.0	3.5	99.3	96.5	1.1	0.2
	1.0	3.0	3.5	99.4	94.1	1.9	0.3
	3.0	3.0	3.8	99.5	96.0	3.6	0.4
	10.0	3.0	2.1	99.0	96.1	7.6	1.5
	16.0	3.0	2.2	97.6	94.4	11.3	1.8
$FeCl_3$	0.1	3.0	4.1	99.3	0.3	1.0	0.2
	1.0	2.9	3.7	98.9	19.2	1.2	0.2
	3.0	2.9	3.3	99.2	8.8	1.9	0.4
	10.0	1.7	1.8	99.0	1.4	8.9	1.4
	20.0	2.0	2.0	98.7	0.1	12.4	2.2
$HgCl_2$	0.1	3.0	3.3	99.9	99.3	1.1	0.3
	1.0	3.0	4.5	98.4	99.8	2.0	0.3
	3.0	3.0	4.4	98.8	98.9	3.7	0.6
	10.0	3.1	2.0	98.4	99.0	8.6	1.7
	20.0	3.0	1.8	92.2	98.6	13.7	2.6
K_2CrO_4	0.1	2.7	3.6	98.1	10.3	0.9	0.2
	1.0	2.1	2.8	76.3	43.4	2.8	0.4
	10.0	2.1	5.0	44.7	31.5	6.7	1.3
Mixture[a]	1.0	2.0	2.3	99.6	b)	6.1	1.0
	5.0	1.8	1.7	98.9	c)	13.8	2.4
	10.0	1.9	1.7	96.8	d)	18.3	2.9

a) A mixture of $CdCl_2$, $PbCl_2$, $FeCl_3$, and $HgCl_2$ solutions was added to a 1.0-matom dm^{-3} Cu(II) solution so that each metal concentration was kept at 1.0, 5.0, or 10.0 matom dm^{-3}. b) Cd 60.0%, Pb 97.5%, Fe 0.8%, and Hg 99.9%. c) Cd 1.1%, Pb 64.3%, Fe 1.4%, and Hg 99.3%. d) Cd 0.3%, Pb 16.2%, Fe 0.6%, and Hg 98.4%.

metallic Cu was insignificant. Since the pH tends to increase during the reaction in the 1.0-matom dm^{-3} solution and hydrolysis of Cu(II) ions occurs from pH *ca.* 5.5, the initial pH was adjusted to 3 excluding the runs for examining acid effects. The sample solutions whose final pH exceeded 6 were acidified to pH *ca.* 3 with HCl and the pH was maintained for a minute before filtration and copper determination. The results are given in Tables 2, 3, and 4.

Of the acids examined here, HNO_3 strongly decreased Cu(II) removal even in small amount. This remarkable interference seems to be related to very low solubility of calcium silicon alloy in HNO_3 solution, possibly due to passivation by a film of silica formed on the solid surface. In the recovery of Hg(II) ions this effect was not so strong,[2] and the reduction rate of Hg(II) ions is greater than that of the film formation. In the HCl, H_2SO_4, and $HClO_4$ solutions, satisfactorily high Cu(II) removal was attained regardless of the acid concentration, because the amount of the alloy added was much greater, in equivalent, than that of Cu(II) ions present in solution. In solutions of high Cu(II) concentrations, the removal percentage will decrease with increasing acid concentration because of significant Ca dissolution. In comparison with the HCl solution, Ca dissolution was smaller in the H_2SO_4 or $HClO_4$ solution, and thus the alloy can be used more effectively for the recovery of Cu(II) ions.

Sodium salts of the conjugate bases of the abovementioned acids were added to 1.0-matom dm^{-3} Cu(II) solutions with varying their concentration from 0.1 to 100 times the Cu(II) concentration. Effects of sodium salts can be considered to be as of the conjugate base ions. Similarly to the above runs in HNO_3, the interference from nitrate ions was significant, becoming appreciable from *ca.* 1 mmol dm^{-3}. Consequently the dissolution of Ca and Si decreased with increasing the salt concentration. When the pH of the 10.0-mmol dm^{-3} $NaNO_3$ solution decreased to 1.0 with HCl, the interference from nitrate ions can be prevented and high Cu(II) removal was attained. The Cu(II) removal, however, did not increase appreciably in the 100.0-mmol dm^{-3} $NaNO_3$ solution even when the pH decreased. The interference from sulfate ions became appreciable from 10.0 mmol dm^{-3}, and also can be prevented by decreasing pH to 1.0. NaCl and $NaClO_4$ did not decrease the Cu(II) removal at any concentration, but the dissolution of Ca and Si increased at high salt concentrations accompanying with an increase in pH.

Effects of metal ions on the reduction of Cu(II) ions are related to their reducibility, and the relative amount of the alloy added to that of the metal ions to be reduced. Since Cd(II) ions are least reducible with the alloy, it gave no appreciable effect on the Cu(II) removal, and thus the Cd(II) removal was low. Pb(II) ions, with lower standard electrode potential than Cu(II) ions, did not affect the Cu(II) removal either, and it was removed with high percentages. High Cu(II) removal was attained in the Fe(III) ion solutions. As shown previously,[1] Fe(III) ions are reduced to Fe(II) ions with the alloy, and the Fe(III) removal seems to be due to hydrolysis. Cu(II) removal decreased with increasing Hg(II) concentration, and Hg(II) ions, one of the most reducible ions, were removed with higher percentages than Cu(II) ions. Dichromate ions, having the highest standard electrode potential among the metal ions examined here, strongly suppressed the Cu(II) removal, whereas the dichromate removal was not so high, since they are efficiently reduced only in strong acid solutions and removed as Cr_2O_3(hydrated) and $CaCrO_4$.[1] Finally mixtures of Cd(II), Pb(II), Fe(III), and Hg(II) ions with various concentrations were added to a 1.0-matom dm^{-3} Cu(II) solution. In the 1.0-matom dm^{-3} metal solution, the highest removal was attained for each metal except for Fe(III). In the 5.0- and 10.0- matom dm^{-3} metal solutions, removal of the respective metal ions was in the order of increasing standard electrode potential. Thus when the concentration of a metal ion to be reduced increases in comparison to that of added calcium silicon alloy, its removal is strongly dependent on its standard electrode potentials, *i.e.* its reducibility.

References

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