CHAPTER VI

RECOVERY OF MIXED METALS BY ELECTROCHEMICAL TECHNIQUE

In previous chapters, experiments were performed with single metal (copper, chromium and nickel) in synthetic solutions. In this chapter, experiments will be tested with mixed metals in both synthetic solutions and effluents from electroplating industry. The experimental set up has been shown in Chapter III (Figure III.5). The reactor is composed of anionic membrane type IONAC, two circulating pumps and a power supply. For each batch, the experiment was separated into two zones, deposition and precipitation zone. First, the experiment was done to recover copper at its optimum current density (10 A/m^2) with constant electrolyte flow rate. After, the current density was being adjusted in order to precipitate other metals in solution such chromium, nickel or zinc. The following part will present results of this study.

1. Recovery of mixed metals in synthetic solution

Synthetic mixed metals solution was prepared at concentration of 1 g/l of each metal (solution S13) and at pH = 1. The flow rate of electrolyte was fixed at 0.42 l/min. For each experiment, two values of current density were applied. The first was 10 A/m^2 to recover copper in metallic state. The another was 90 A/m^2 to precipitate other metals contained in solution. The solution conductivity was kept constant around 20 - 40 mS/cm by adding 5 % by weight of Na_2SO_4.

1.1 Results of mixed metals solution of chromium, nickel and zinc

This experiment was performed in order to test the possibility of three metals precipitation including chromium, nickel and zinc. Figure VI.1 presents percentage of metal recovery as a function of electrolysis time at current density of 90 A/m^2 and electrolyte flow rate of 0.42 l/min.

These results showed that three metals can be precipitated and completely recovered in 9 hours. Zinc was recovered first, it started at the 5th hour and complete at the 9th hour. The percentage of chromium and nickel started to change at the 6th hour and stopped at the 9th hour. More than 99.9 % of all metals was recovered with outlet concentration less than 1 mg/l. The pH evolution increased in cathodic compartment and decreased in the anodic compartment following the reaction presented in Chapter II. pH in the cathodic compartment started to change during 6 - 7 hours. It inferred that, zinc is recovered by deposition in the first 6th hours and after that, it is removed by precipitation when solution pH was increased. The change of recovery percentage of chromium and nickel was not observed before the 6th hour. It indicated that no deposition of chromium and nickel occurs.

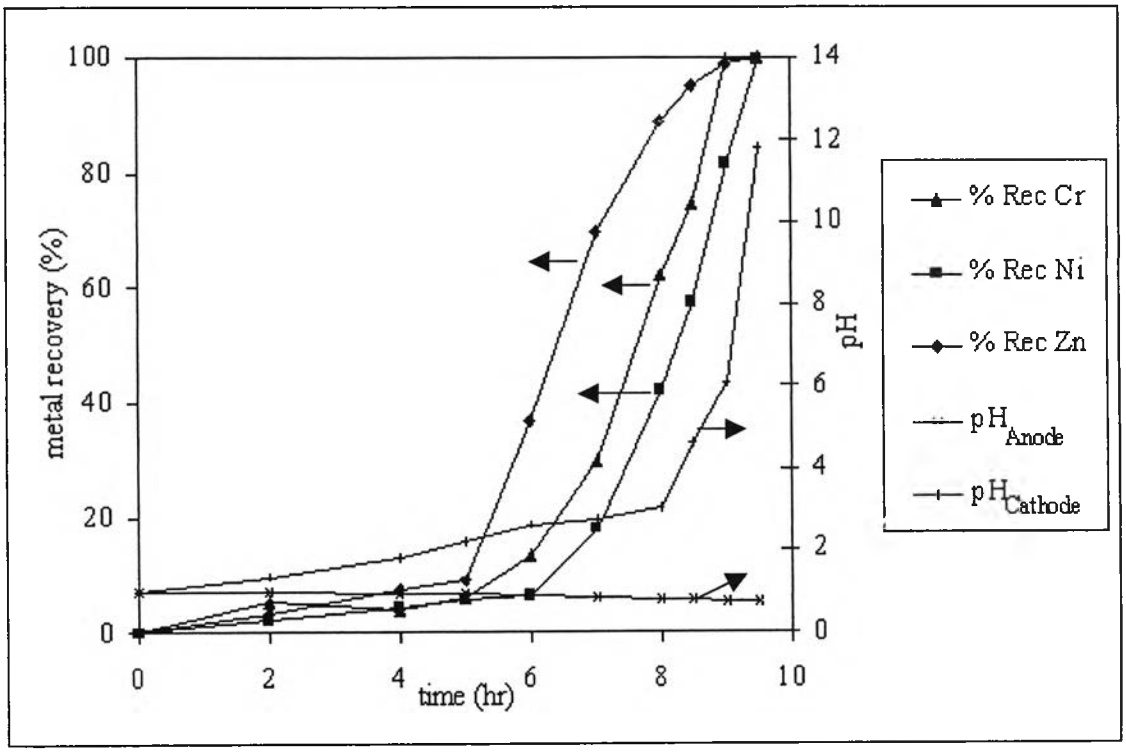

Figure VI.1: Metal recovery percentage and pH evolution versus time (solution S13).

1.2 Results of mixed metals solution of copper, chromium, nickel and zinc

The experiment was run with current density of 10 A/m^2 and 90 A/m^2 in mixed metals synthetic solution of copper, chromium, nickel and zinc (solution S14) at constant electrolyte flow rate (0.42 l/min). The pH of solution was adjusted by H_2SO_4 to pH = 1.

Figure VI.2 depicts the results of this study. The copper was recovered as a polynomial form during 5 hours of electrolysis time whereas concentrations of chromium, nickel and zinc had little change. More than 98.9 % of copper was deposited at current density of 10 A/m^2. After that, the current density was adjusted to around 90 A/m^2. Chromium, nickel and zinc started to precipitate after 10 hours electrolysis time corresponding to the increasing of pH in the cathodic compartment. More than 99 % of all metals was recovered within 13 - 13.5 hours. After the treatment, the outlet concentrations of copper, chromium, nickel and zinc were respectively about 0.13, 1.00, 1.43 and 0.61 mg/l.

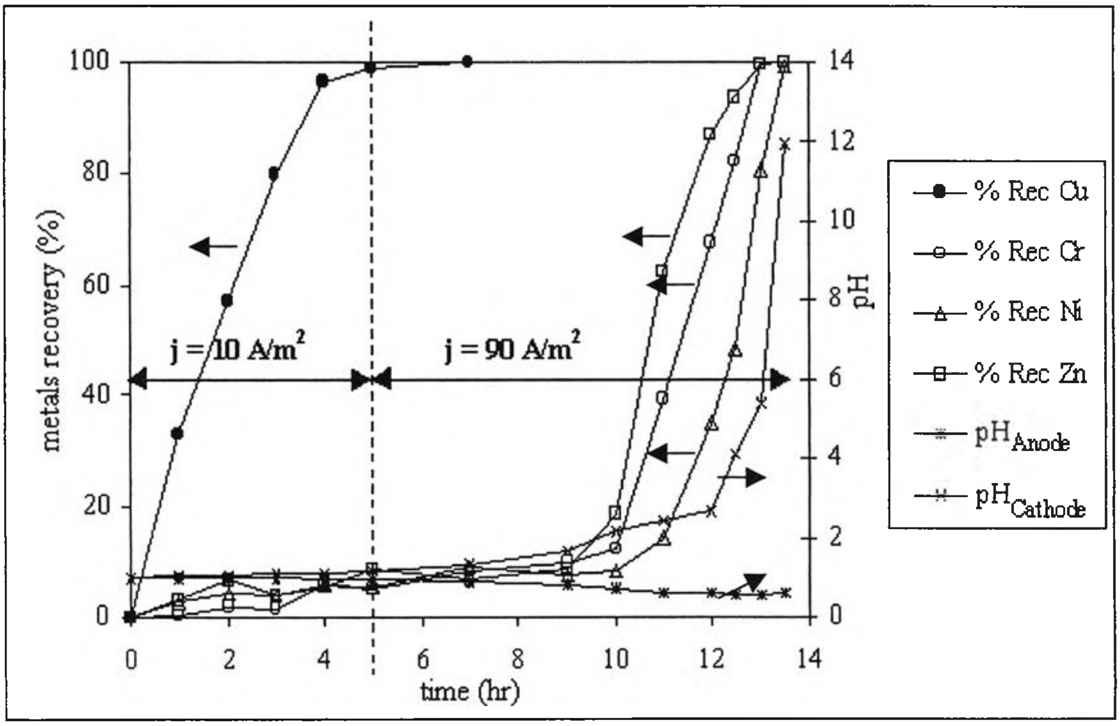

Figure VI.2: Metal recovery percentage and pH evolution versus time (solution S14).

From this study, mixed metals in synthetic solution is successfully recovered in reactor with membrane with high metal recovery percentage. In the next part, the experiment was carried out with effluent solution from electroplating industry.

2. Recovery of mixed metals from electroplating effluent

Two types of electroplating effluent from two companies were included in this study. They were Genco Co., Ltd. (Plant I) and Endo Thai Co., Ltd. (Plant II). The experimental procedure was carried out similar to that of mixed metals synthetic solution. Table VI.1 shows the characteristics of effluent solution from Plant I (solution S15) and Plant II (solution S16).

The solution of Plant I contains low metal concentrations. It is composted of copper, chromium, nickel and zinc in acid solution with light yellow colour. However, for plant II, metal concentrations are higher and each metal is also found separately. It is composted of copper, chromium and nickel in acid state.

Experiments were performed at current density of 10 A/m^2 and 90 A/m^2 for copper, chromium and nickel recovery with constant electrolyte flow rate (0.42 l/min).

Table VI.1: Characteristics of effluent solution from Plant I and Plant II.

	Plant I (Solution S15)	Plant II (Solution S16)
pH	2.23	2.34
Copper (mg/l) Chromium (mg/l) Nickel (mg/l) Zinc (mg/l)	283 220 128 106	5,592 1,425 3,113 No
Colour	Light yellow	Copper solution : Light blue colour Chromium solution : Yellowish orange colour Nickel solution : Light green colour

2.1 Results of mixed metals solution from Plant I and Plant II

The experiment for the Plant I solution (solution S15) has been performed at constant electrolyte flow rate at current densities of 10 A/m^2 and 90 A/m^2. The solution pH was adjusted to around 1 by adding H_2SO_4. The solution conductivity was kept constant around 20 - 40 mS/cm by adding Na_2SO_4 (5 % by weight).

Figure VI.3 demonstrates the percentage of copper recovery from effluent solution of Plant I. It increased as polynomial form during the first 6 hours of electrolysis time at current density of 10 A/m^2 whereas the recovery percentage of other metals increased slowly with about 5 - 15 %. At this period, more than 99 % of copper was recovered at the 4th hour and the outlet concentration is less than 1.09 mg/l. The change of chromium recovery is suggested due to the loss of chromium as anionic species to anodic compartment whereas the change of nickel is coming from little deposition on cathode surface. After the 6th hour, the current density was adjusted to 90 A/m^2. The recovery percentage of chromium, nickel and zinc was increased rapidly which is corresponding to the increasing of pH in the cathodic compartment. More than 99.9 % of all metals was removed after 8.5 hours. After the process, outlet concentrations of copper, chromium, nickel and zinc were respectively around 0.13, 0.20, 0.33 and 0.05 mg/l.

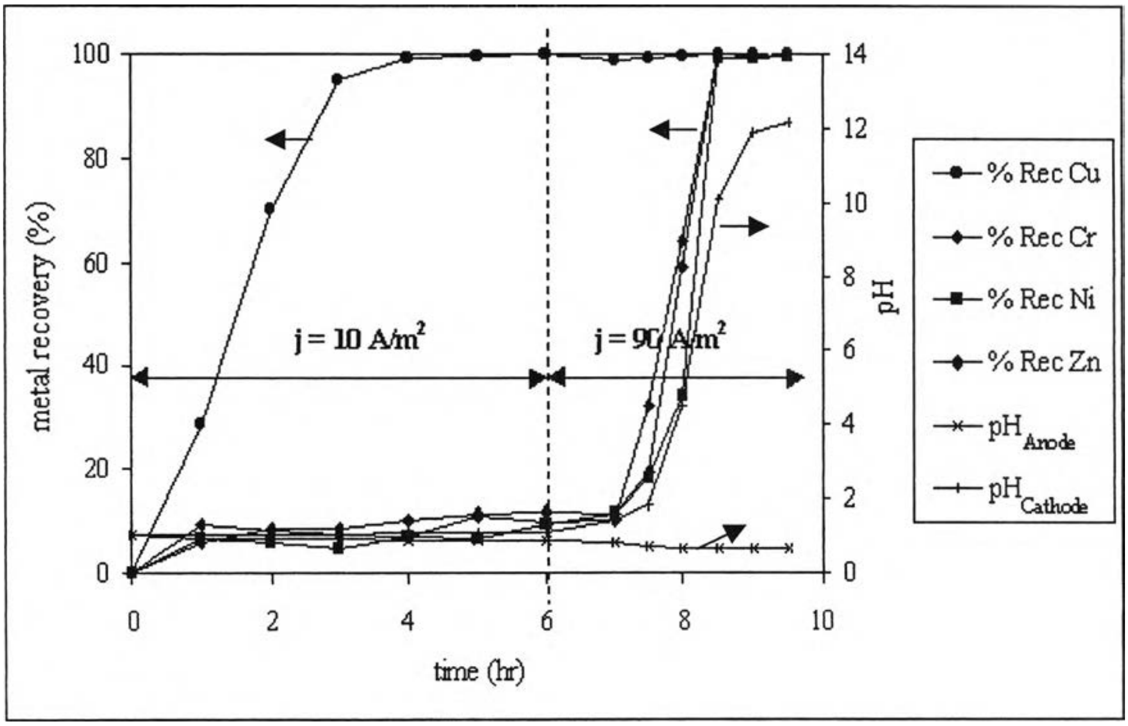

Figure VI.3: Metal recovery percentage and pH evolution versus time (solution S15).

The solution of each metal from the second electroplating plant (solution S16) was mixed to the preferable concentration of 932, 964, and 468 mg/l for copper, chromium, and nickel, respectively. pH of solution was adjusted to around 1 by H_2SO_4. Conductivity was fixed around 20 - 40 mS/cm.

Figure VI.4 shows the results of metal recovery from Plant II solution. The deposition of copper increased slowly at the beginning up to the 6th hours, it increased rapidly. More than 99 % of copper was recovered in 12 hours whereas the recovery percentage of chromium and nickel slightly changed. This is due to the loss of chromium to anodic compartment as anionic species and the deposition process of nickel. After 12 hours, the current density was changed to 90 A/m^2. During this period, both chromium and nickel reacted with hydroxide ions and precipitated rapidly. The precipitation started at 13.5 hours with corresponding to the increasing of solution pH. More than 99.9% of chromium and nickel was recovered in 15 hours. The remaining concentrations of copper, chromium and nickel in treated solution were lower than 0.01, 0.19 and 0.05 mg/l, respectively.

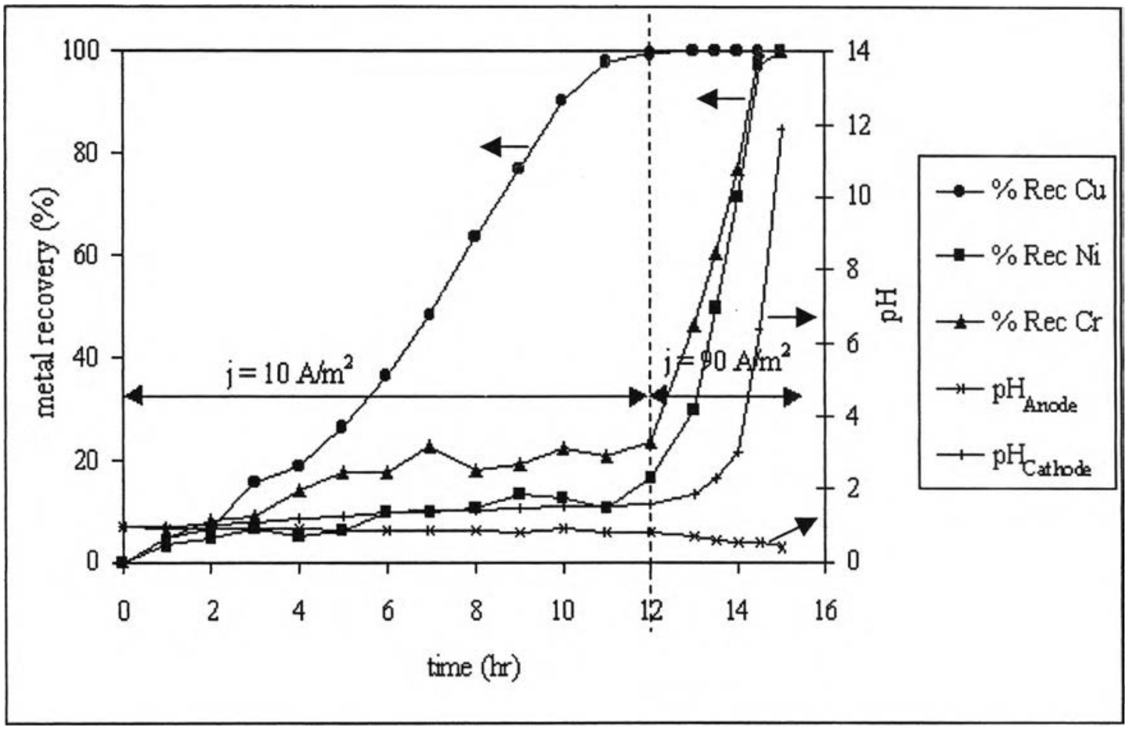

Figure VI.4: Metal recovery percentage and pH evolution versus time (solution S16) [Cu] = 932 mg/l, [Cu] = 964 mg/l and [Ni] = 468 mg/l, pH = 1.

Table VI.2 summarizes the initial and final concentration, electrolysis time of the process of synthetic solution, Plant I and Plant II solutions. The difference of total electrolysis time between synthetic and Plant I solution is coming from the difference in initial metal concentrations and composition of solutions. The initial metal concentrations and total electrolysis time of synthetic solution are nearly the same to those of Plant II solution. However, the complete electrolysis time of copper has about 2.4 times difference. This difference will be investigated and shown in the next part.

Table VI.2: Summation characteristics of synthetic, Plant I and Plant II solutions.

	Synthetic solution	Plant I solution	Plant II solution
Initial concentration (mg/l)			
Copper	1,014	283	932
Chromium	985	220	964
Nickel	1,128	128	468
Zinc	1,087	106	No
Final concentration (mg/l)			
Copper	0.13	0.13	0.01
Chromium	1.00	0.20	0.19
Nickel	8.43	0.33	0.05
Zinc	0.61	0.05	No
Electrolysis time for copper recovery	5	6	12
Total electrolysis time	13.5	8.5	15

3. Effect of parameters on copper recovery

3.1 Effect of cyanide compound

The first interested parameter on copper recovery was a presence of cyanide compound in the effluent solution. The contamination of cyanide compound in solution strongly affect electrochemical technique. The cyanide compound is generally presented as anionic compound and it can be partially oxidized during the process. So some parts of applied current will lose by cyanide reduction.

The test of cyanide compound was performed by the analytical method called "Prussian Blue Test". Experiments were performed with distillated water as a blank solution and potassium cyanide (KCN) to see the positive test and to compare with the results of the Plant I and Plant II solution. Table VI.3 shows the results of cyanide test.

Table VI.3: Results of cyanide test by Prussian Blue Test method.

Sample	Colour after test	Result
Blank (Distillated water)	Light yellowish red colour	Negative test
Potassium cyanide (KCN)	Deep blue colour and sludge	Positive test
Plant I solution	Light yellowish red colour	Negative test
Plant II solution	Light yellowish red colour	Negative test

Potassium cyanide shows the positive test as deep blue colour and sludge. This colour and sludge are coming from the cyanide compound ($KFe[Fe(CN)_6]$. On the other hand, the blank, Plant I and Plant II solution showed the negative test with light yellowish red colour. This colour is coming from the colour of ferricchloride ($FeCl_3$). From this test, it demonstrates that the Plant I and Plant II solution had no cyanide compound. So the previous difference do not come from the effect of cyanide compound.

3.2 Effect of brightener

In electroplating process, a brightener is generally added in the plating bath in order to increase the brightness on the surface of specimen. However, it has both advantages and disadvantages. If the quantity of brightener added is too low, the brightness on the specimen surface is also low. If high quantity of brightener is added, the surface is easily broken. Nevertheless, this properties depend upon other effects such as applied current density, type of brightener.

In this study, three types of brightener were introduced to investigate their effect on copper recovery. Table VI.4 shows the composition of the brighteners [Okuno Chemical Industries Co., Ltd.]. Experiments were performed with synthetic solution of copper with concentration about 1,000 mg/l for pH = 1 (solution S1) at current density of 10 A/m^2 and constant electrolyte flow rate. In each experiment, 0.15 % (by volume) of brightener was added in the solution.

Table VI.4: Composition of brightener.

Type of brightener	Color	Content	Weight (%)
Elecopper 25A	Deep reddish violet colour liquid	Di - Methyl Safranine T type Dry Thioflavine De - Ionized Water	10.0 0.5 89.5
Elecopper 25B	Light blue colour transparent liquid	Polyethylene Glycol 6000 Sodium 3-Mercaptopropylsulfonate Copper Sulfate De - Ionized Water	8.0 1.2 0.5 90.3
Elecopper 25MU	Light yellowish green colour transparent liquid	Polyethylene Glycol 6000 Copper Sulfate Thioflavine De - Ionized Water	4.0 1.0 0.5 94.5

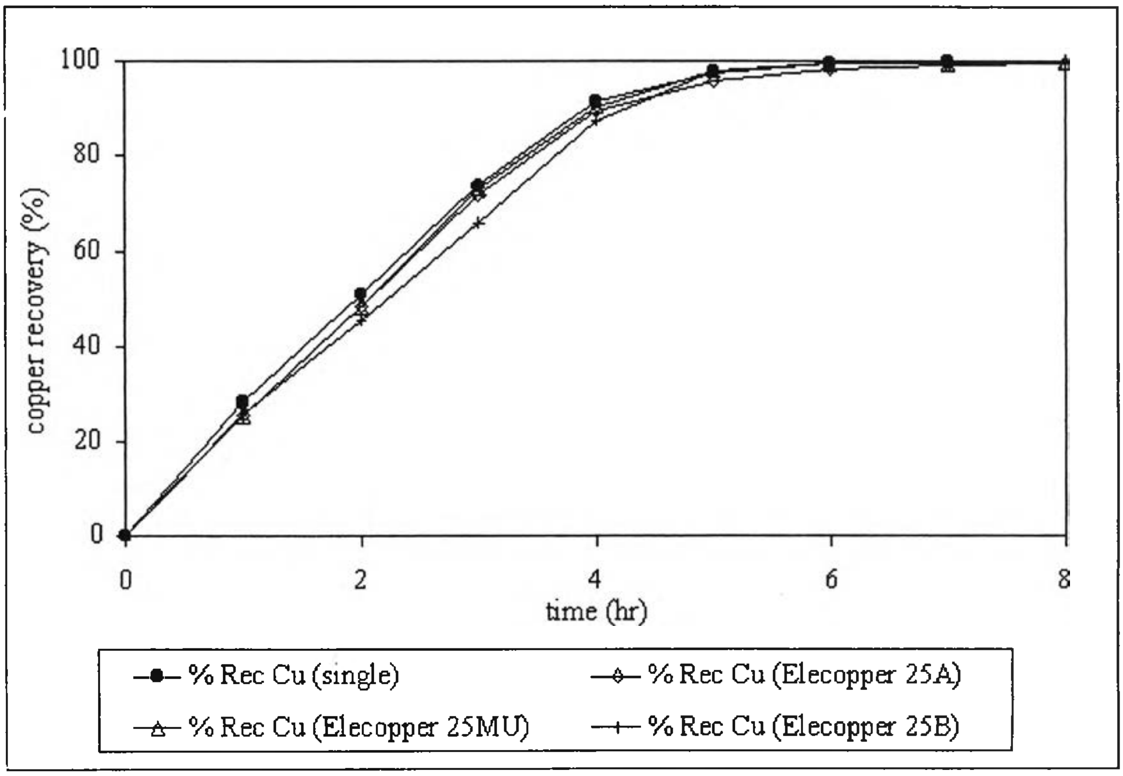

Figure VI.5: Copper recovery percentage versus time in a presence of brightener.

The correlation between percentage of copper recovery versus electrolysis time in a presence of brightener is shown in Figure VI.5. The copper solutions contained some brighteners gave the same copper recovery percentage as the single copper solution. More than 99 % of copper was recovered in 6 hours with more than 60 % current efficiency. So we can said that the brightener composed of Elecopper 25A, Elecopper 25MU and Elecopper 25B has no effect on copper recovery.

3.3 Effect of nickel and chromium in the system

The effluent solution from Plant II was used in this experiment. The solutions of copper, chromium and nickel were mixed to obtain the preferable concentration. Experiments were performed under the optimum current density of copper (10 A/m^2) with constant flow rate of electrolyte and they were separated into three parts. The first experiment was done with single copper solution ([Cu] = 475 mg/l). The second was performed with the mixed solution of copper and chromium solution ([Cu] = 496 mg/l, [Cr] = 523 mg/l) and the last was made with the mixed solution of copper and nickel (([Cu] = 514 mg/l, [Ni] = 485 mg/l). The pH of solution was adjusted by H_2SO_4 to pH = 1.

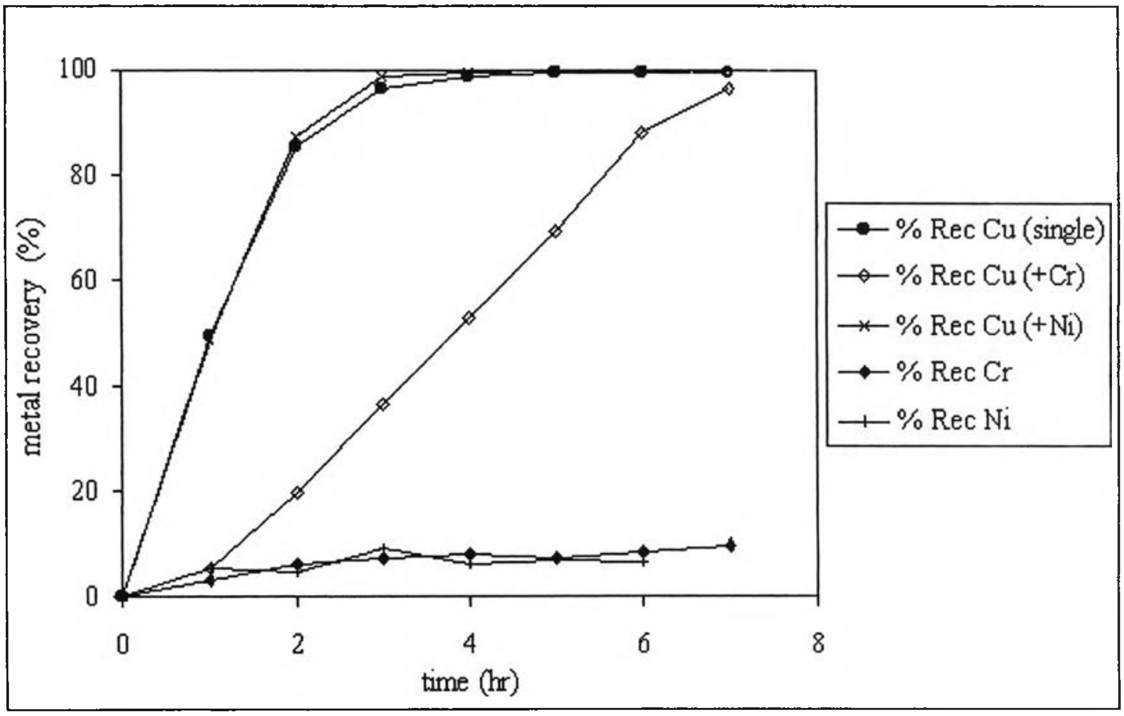

Figure VI.6: Copper recovery percentage versus time (solution S16).

([Cu] = 475 mg/l, [Cr] = 523 mg/l and [Ni] = 485 mg/l, pH = 1).

Figure VI.6 presents the percentage of copper recovery versus electrolysis time in a presence of chromium and nickel. It shows that the solution in a presence of nickel gave the copper recovery evolution similar to the single copper solution. More than 99 % of copper was recovered in 4 hours and the nickel recovery percentage had a little change due to the deposition during the process. On the other hand, the percentage of copper recovery was only 53 % in 4 hours of electrolysis time and about 96 % in 7 hours in a presence of chromium. The chromium recovery percentage had a little change due to the loss of chromium as anionic species to the anodic compartment during the process. From this study, it indicates that chromium has a strong effect on copper recovery.

From the previous study of synthetic mixed metals solution, chromium in trivalent form ($CrK(SO_4)_2 \cdot 12H_2O$) in the solution has no effect on copper recovery. However, in experiment with effluent solution, chromium ion had an effect on copper recovery. It implies that the chromium in effluent solution should be presented in hexavalent form (Cr^{6+}).

In order to test this hypothesis, the experiment was performed with the procedure shown in Appendix B.3. The positive test shows the light blue colour of chromium pentoxide (CrO_5) in amyl alcohol layer. The elementary reaction can be expressed by

$$H_2Cr_2O_7 + 4H_2O_2 + H_2SO_4 \longrightarrow K_2SO_4 + 2CrO_5 + 5H_2O \qquad (VI.1)$$

The blue solution is not stable, it will decompose to green colour solution of chromic salts and oxygen gas. This test shows that chromium contained in effluent solution from electroplating industry is presented in hexavalent form (Table VI.5). The reactions in the system can be expressed by the following reactions.

Reactions in the cathodic compartment

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad E^0 = 1.33 \text{ V/NHE} \qquad (VI.2)$$

$$HCrO_4^- + 7H^+ + 3e^- - \longrightarrow Cr^{3+} + 4H_2O \quad E^0 = 1.195 \text{ V/NHE} \qquad (VI.3)$$

$$Cu^{2+} + 2e^- \longrightarrow Cu \quad E^0 = 0.340 \text{ V/NHE} \qquad (VI.4)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad E^0 = 0 \text{ V/NHE} \qquad \text{(VI.5)}$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad E^0 = -0.83 \text{ V/NHE} \qquad \text{(VI.6)}$$

$$Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3 \qquad E^0 = 1.3 \text{ V/NHE} \qquad \text{(VI.7)}$$

Reaction in the anodic compartment

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \; E^0 = -1.23 \text{ V/NHE} \qquad \text{(VI.8)}$$

Table VI.5: Results of hexavalent chromium test.

Sample	Colour after test	Result
Blank (Distillated water)	Light colour	Negative test
Potassium dichromate ($K_2Cr_2O_7$)	Light blue colour in amyl alcohol	Positive test
Chromium (III) potassium sulphate $CrK(SO_4)_2.12H_2O$	Dark blue colour	Negative test
Plant I solution	Light blue colour in amyl alcohol	Positive test
Plant II solution	Light blue colour in amyl alcohol	Positive test

Between pH = 1 and pH = 6, hexavalent chromium is presented in solution as $Cr_2O_7^{2-}$ and $HCrO_4^-$ [47]. The reductions of hexavalent chromium occur when the current is applied. The colour of solution is changed from hexavalent chromium colour (yellowish orange colour) to the violet blue colour of trivalent chromium as shown by equations (VI.2) and (VI.3). This colour change is obviously observed during the experiment. At the same period, the reduction of copper ions to metallic copper occurs as equation (VI.4). However, the reduction of hexavalent chromium to trivalent chromium is higher than the reduction of copper ions to metallic copper because standard potential of the copper reduction is lower than that of chromium reduction. The other reactions observed in cathodic compartment are reduction of proton and water to hydrogen gas and hydroxide ions as equation (VI.5) and equation (VI.6). The precipitation of trivalent chromium with hydroxide ions produced as equation (VI.6) occurs after the reduction of hexavalent chromium completes as shown by equation (VI.7). In the anodic compartment, the oxidation of water to oxygen gas and proton is observed similar to the previous experiments.

3.4 Effect of hexavalent chromium concentration

Experiments were done with effluent solution from Plant II at current density of 10 A/m^2 and constant electrolyte flow rate. Eight different concentrations (51, 105, 188, 405, 633, 847, 1,009 and 1,338 mg/l) of chromium solution presented in hexavalent form were added in the solution with copper concentration of 984 mg/l. The pH of all mixed solutions was adjusted to pH around 1.

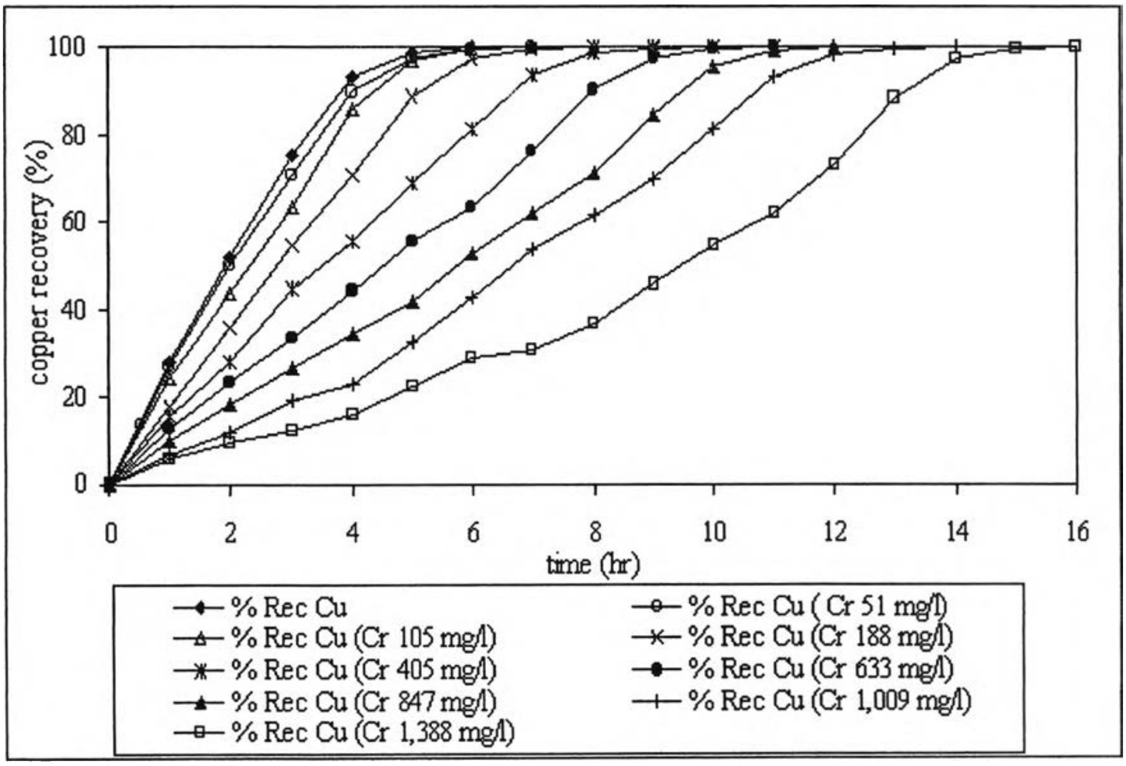

Figure VI.7: Copper recovery percentage versus time in a presence of several chromium concentrations (solution S16).

Figure VI.7 shows the plot of copper recovery percentage in cathodic compartment versus electrolysis time in a presence of hexavalent chromium at different concentrations. For single copper solution, more than 99 % of copper was recovered in 6 hours with current efficiency more than 90 % at 80 % recovery.

However, in a presence of hexavalent chromium, the percentage of copper recovery was an inverse function with the hexavalent chromium concentration. Their effect was initially observed after more than 100 mg/l of chromium presented in the solution.

Figure VI.8 shows the current efficiency of copper recovery and electrolysis time as a function of initial hexavalent chromium concentration. It showed the current efficiency decreased with increasing concentration of hexavalent chromium. At chromium concentration less than 600 mg/l, increasing of chromium by 2 times decreased current efficiency of copper recovery approximately 0.89 times. On the other hand, the increasing of chromium about 1.37 times led to the decreasing of current efficiency of copper recovery 0.86 times at chromium concentration more than 600 mg/l. Furthermore, an electrolysis time is direct proportion to the increasing of initial hexavalent chromium concentration. The increasing 2 times of initial hexavalent chromium concentration will increase about 1.40 times electrolysis time.

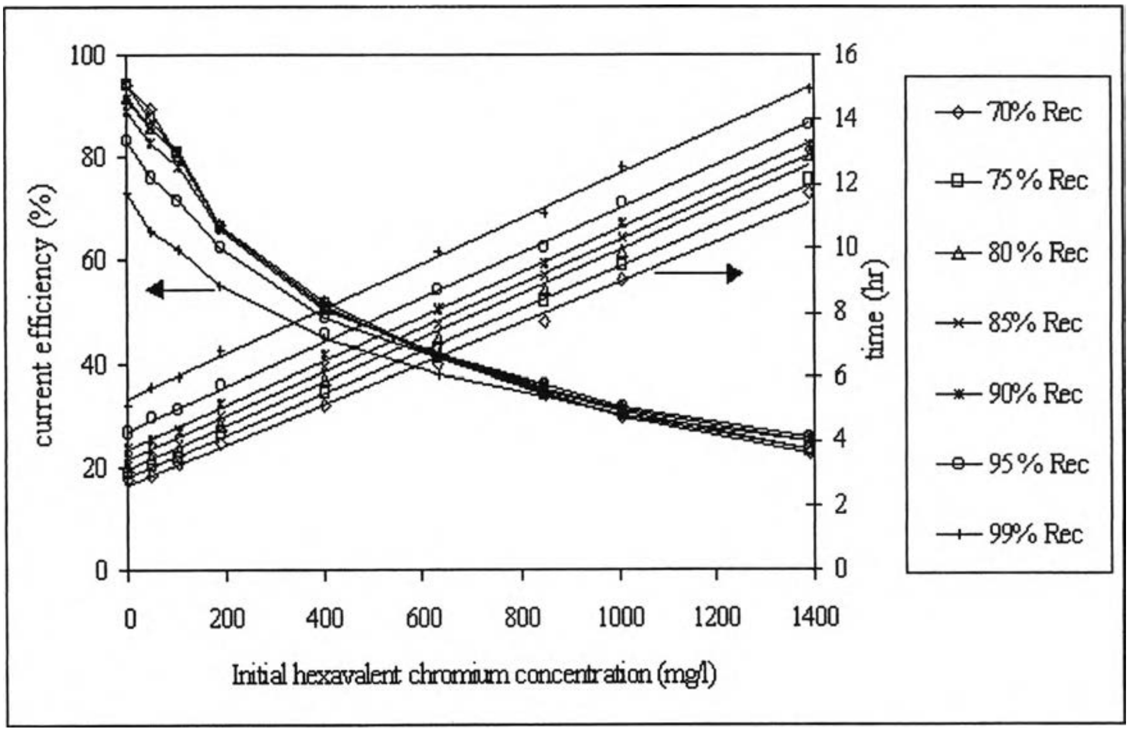

Figure VI.8: Current efficiency and time versus initial hexavalent chromium concentration (solution S16).

At 99 % copper recovery, the equation of current efficiency and electrolysis time as a function of initial hexavalent chromium concentration was expressed by

Current efficiency equation (ϕ)

$$\phi = 3\times10^{-5}[Cr]^2 - 0.0659[Cr] + 69.437 \qquad \text{(VI.9)}$$

Electrolysis time equation (t)

$$t = 0.007[Cr] + 5.323 \qquad \text{(VI.10)}$$

Both equations (VI.9) and (VI.10) is sufficient to predict the current efficiency and electrolysis time at 99 % copper recovery when the solution contains copper concentration about 1,000 mg/l.

4. Cost analysis of mixed metals recovery from electroplating industry

The cost analysis for treatment of effluents from Plant I and Plant II was studied and the results were shown in Table VI.6. The total operating cost of effluent from Plant I was lower than the effluent from Plant II (about 8 %) because of the low amount of heavy metals content, so it causes the complete recovery in the shorter time. The copper ions in solution were removed as a valuable metal, so it can be sold. The chromium, zinc and nickel were removed as a mixed precipitated sludge. It is impossible to separate, so the landfill process is a disposal option and its cost is shown in the below table. Nevertheless, the decision making to select the sludge treatment procedure depends upon the economic reason.

Table VI.7 shows the comparison of operating costs of this work with the other two previous works. The results demonstrate that all treatment processes have almost the same operating costs. However, our operation should be easier than the others. In addition, our work succeeds to recover many metals (copper, chromium, nickel, and zinc), whereas only one metal (chromium) was removed by the two other works.

Table VI.6: Cost analysis of metal recovery from Plant I and Plant II solutions.

	Plant I			Plant II		
	Cu	Cr, Ni, Zn	Total	Cu	Cr, Ni	Total
Power consumption (kW-hr / m^3)	3.96	77.50	81.46	7.92	93.00	100.9
Electricity cost (Baht / m^3)	11.30	221.90	233.2	22.68	266.26	288.9
Recovery weight (kg / m^3)	0.283	0.796		0.929	2.647	
Recovery cost (Baht / m^3) (59.42 Baht / kg - Cu)	16.79			55.21		
Landfill cost (Baht/m^3) (0.874 Baht / kg - sludge)		0.697			2.313	
Total operating cost (Baht / m^3)	217.10			236.04		
or in US$ /m^3 (1 US$ = 43.5 Baht)	4.99			5.43		

Table VI.7: Comparison of operating costs of this work and conventional methods.

Treatment process	Operating cost (US$/m^3)
This work	
- Plant I	4.99
- Plant II	5.43
Precipitation process [67]	5.71
Ion exchange process [68]	5.29

5. Conclusion

An electrochemical technique was applied to recover mixed metals (copper, chromium, nickel and zinc) from synthetic solution and the effluent from electroplating industry. The experiments were performed in a reactor with an anionic membrane at constant flow rate of electrolyte. The total electrolysis time was separated into two periods. The first period was used to recover copper by electrodeposition technique and the second period was used to remove chromium, nickel and zinc by electroprecipitation technique.

The first part of experiments was studied by using synthetic mixed metals solution to test the possibility of mixed metals recovery. The results showed that copper was recovered by electrodeposition technique with a good recovery percentage and a current efficiency after 5 hours. More than 99 % of copper was recovered after 4 hours with outlet concentration of less than 1.09 mg/l. The other metals contained in the solution were recovered by precipitation. More than 99 % was recovered in 8.5 hours later.

In the next part, experiments were applied to two electroplating effluents (Plant I and Plant II solutions). The Plant I solution contained low metal concentration (< 300 mg/l) while the Plant II solution contained high metal concentration (> 1,000 mg/l). The results of the Plant I solution were nearly the same as those of synthetic solution. The copper was completely recovered in 6 hours and the complete precipitation process was reached after 8.5 hours. However, the different results were obtained by using the Plant II solution. The complete electrolysis time of copper recovery by using this solution was 2.4 times higher than the copper recovery from synthetic solution, and then the other metals contained in the solution were completely recovered after 13.5 hours.

The effect of some parameters on copper recovery was investigated. There were an effect of cyanide compound, an effect of brightener, an effect of nickel and chromium in the system, and an effect of hexavalent chromium. It found that cyanide compounds don't present in the solution, and the brightener (including Elecopper 25A, Elecopper 25MU, Elecopper 25B) had no effect on copper recovery. The recovery percentage of solution in a presence of brightener had the same recovery percentage as a single copper solution. In addition, nickel presented in the solution had no effect on copper recovery. However, chromium in hexavalent form had a strong effect on copper recovery.

Higher concentration of hexavalent chromium would increase the total electrolysis time and decrease the current efficiency of copper recovery. A presence of hexavalent chromium retarded the copper reduction reaction because hexavalent chromium has a standard half - cell potential of a reduction reaction higher than that of copper. The reasonable operating cost was obtained in this process, and the high quantity of copper in solution will reduce the total operating cost.

Metals in electroplating effluents are completely recovered by electrodeposition technique and electroprecipitation technique. It is recommended that an actual operation should be performed with continuous process and high initial pH solution. However, some limitation should be considered carefully such as initial pH solution. Roberts et al [45] discovered that the suitable pH for hexavalent chromium reduction should be less than 3.5. If a very high initial pH solution is used, the reduction of hexavalent chromium to trivalent chromium is poor. On the other hand, if a very low initial pH solution is used, the long electrolysis time is needed.

GENERAL CONCLUSION

Heavy metals such as copper, chromium and nickel were successfully recovered from synthetic solution and electroplating effluent by using electrochemical technique.

The polarization curves conducted by potentiostat and microbalance technique were chosen to test the possibility of metal removal and to define the potential range. The optimum potential range of copper reduction was between -350 mV/SCE to -170 mV/SCE. In case of chromium and nickel, the reduction peak was insignificant observed due to the reduction peak of water and proton. By this reason, the electrodeposition technique is then appreciated to copper recovery while the electroprecipitation technique is applied to recover chromium and nickel.

The results of copper recovery by using a simple batch reactor with plane electrode and by using a 3PE reactor with graphite particle electrode gave a high current efficiency. In a simple batch reactor, the optimum operating condition was found at current density of 10 A/m^2 with either low initial pH (pH = 1) or high one (pH = 5) for a concentration of 1 g/l. More than 90 % of copper was recovered within 6 hours with current efficiency more than 90 % at 70 % recovery. In the case of holding pH at 1 and changing copper concentration from 1 g/l to 5 g/l, the optimum current density was around 25 - 33 A/m^2. More than 95 % of copper was deposited on a cathode surface within 10 hours with 85 % current efficiency. The mass transfer coefficient, which is strongly depended upon the flow rate of electrolyte, was determined by applying a developed model. The model was expressed in terms of dimensionless numbers. The mass transfer coefficient obtained in this current work was higher than that of other literatures because of different geometry of the reactor. At high metal concentrations, the kinetic reaction was controlled by charge transfer, whereas it was controlled by mass transfer at low metal concentrations.

In a 3PE reactor, the experiments permitted to estimate the effect of current intensity, air pulse frequency, cathode material type, and flow rate of electrolyte on copper recovery. The optimum condition was found when applying 9 A current intensity which is corresponding to the lowest operating cost of 1.97 US$/m^3. The total electrolysis time was 7 hours with more than 30 % current efficiency. The percentage of copper recovery was an inverse function with air pulse frequency due to the current intensity drop in the destabilization period. The same behaviour was observed when experiments performed with graphite and graphite covered by copper because the copper deposition on graphite is very quick and consequently works as graphite initially covered by copper.

Chromium and nickel were recovered in a classical reactor with anionic membrane by electroprecipitation technique. The electrolysis time was an inverse function with current density. The optimum current density for both metals was found at current density of 90 A/m^2. High initial pH solution was required a short electrolysis time which is corresponding to lower operating cost. The model used to predict the pH evolution in the cathodic compartment indicates that the model with a loss flux of hydroxide ions gives a good fitting with experimental pH evolution. The effect of loss of hydroxide ions was markedly observed when a lower initial pH solution was studied. There is no this effect when a higher initial pH solution (pH = 5) was used.

In the last chapter, the experiment was conducted to recover metals from synthetic mixed solution and electroplating effluents based on the optimum condition of single metal from synthetic solutions. The results of mixed metal recovery from synthetic solutions indicated that copper was recovered with high current efficiency. More than 99 % of copper was recovered in 4 hours and outlet concentration was lower than 1.1 mg/l. The other metals contained in solutions were recovered more than 99 % in next 8.5 hours later.

For the results of electroplating effluent, higher electrolysis time was observed for copper recovery due to a presence of hexavalent chromium (Cr^{6+}) in the solution. This effect was initially observed at a concentration of hexavalent chromium higher than 100 mg/l. The electrolysis time of copper recovery is a direct function with hexavalent chromium concentration. The reduction of hexavalent chromium to trivalent chromium has higher standard half - cell potential than copper reduction. It is a competitive reaction with the copper reduction. The major part of applied current is used for chromium reduction and the residual part is used for copper reduction.

In conclusion, metals contained in synthetic and electroplating solutions were successfully recovered by applying electrochemical techniques. The optimum conditions for copper, chromium and nickel were determined. The concentration models and dimensionless numbers were developed in the copper recovery system. pH evolution model in the cathodic compartment was developed in chromium and nickel recovery system. These model and dimensionless number can be used as a fundamental data for the further study of wastewater treatment by using electrochemical technique. For the future work, experiments should be carried out as follows.

1. From the optimum condition of this work, scale up of electrochemical reactor should be accomplished.
2. Electrochemical technique should be applied with other kinds of wastewater such as organic wastewater.