2. EXPERIMENTAL

2.1 Chemicals & materials

Chemical	Source
Analytical Grade cupric (II) chloride dihydrate	Ajax Chemical (Sydney)
Analytical Grade nickel (II) chloride hexahydrate	Ajax Chemical (Sydney)
GPR Grade nickel (II) sulphate hexahydrate	BDH Laboratory Supplies
GPR general grade chromium trioxide	Hopkin & Williams LTD
AnalaR Grade potassium chloride	BDH Laboratory Supplies
AnalaR grade sodium hydroxide	Hopkin & Williams LTD
Analytical Grade Sodium chloride (preheated at 110°C for an hour to removed moisture)	Riedel-de Haen

Water: Doubly-distilled water (from an all-glass distillation apparatus) was used in all solution preparations and for final rinsing.

pH standard solutions: Referee Precision pH Buffer, pH (7.000 ± 0.002 @ 25 °C) and pH (4.000 ± 0.002 @ 25 °C) manufactured by Analytical Products, Inc. was used for pH electrode calibration.

Stainless steel electrodes: Commercial stainless steel plates (0.5 mm thick), trade code AISI 304 obtained from EU Master Stainless Steel Engineering Works, Kuala Lumpur, Malaysia, was used for all tests throughout the project.

Aluminium electrodes: Commercial aluminium plates (0.5 mm thick), trade code UNS A91100 (AA Designation 1100) obtained from EU Master Stainless Steel Engineering Works, Kuala Lumpur, Malaysia, was used for all tests throughout the project.

Composition specification for these two type of electrodes were giving in Table 9. (Appendix 1).

Sulfuric acid: R & M Chemicals analytical grade concentrated sulfuric acid 96% (molarity 18.0)[83] was used as stock solution to prepared the 0.1 M sulfuric acid solution used in the polarization measurements.

Stock solutions for preparing standard solutions for Atomic spectrophotometry: BDH Laboratory Supplies Spectrosol ·1000ppm nickel nitrate; copper (II) nitrate; chromium (III) nitrate {$Cr(NO_3)_3.9H_20$}; iron (III) nitrate {$Fe(NO_3)_3.9H_20$}; in 0.5 M nitric acid, standard solution.

2.2 Apparatus & Equipment

Glassware: All glassware were cleaned by soaking in concentrated chromic acid overnight and then thoroughly washed with large quantities of tap-water before soaking in distilled water.

Storage (sample) bottles and electrolysis tanks: Polyethylene plastic sample bottles were cleaned by prewashing with detergent and soaking in 10% nitric acid overnight. They were then thoroughly washed with large quantities of tap-water, followed by soaking in distilled water overnight, after which they were rinsed with doubly distilled water and allowed to dry in air in an air-conditioned room.

Polarization cell: EG&G Princeton Applied Research Corrosion Testing Cell was used. A photograph of the cell is given in Figure (2). The maximum capacity of the cell is 320 ml. The geometrical surface area of the working (test) electrode was (1.00 +/- 0.05) cm^2. The cell was cleaned with detergent, thoroughly washed with tap-water, and then rinsed with distilled water several times before soaking in doubly distilled water.

A scanning potentiostat/galvanostat model 362, manufactured by EG&G Princeton Applied Research was used to carry out the potentiodynamic sweeps.

A Keithley 575 Measurement and Control System shown in Fig (3) was used for analog and digital interfacing between the scanning potentiostat/galvanostat and a IBM AT compatible microcomputer system. All I-V data were stored in ASCII format files, which could be readily recalled for data treatment on other faster microcomputers.

Reference electrode: A Radiometer saturated calomel electrode model K401 was used as the reference electrode in the polarization cell.

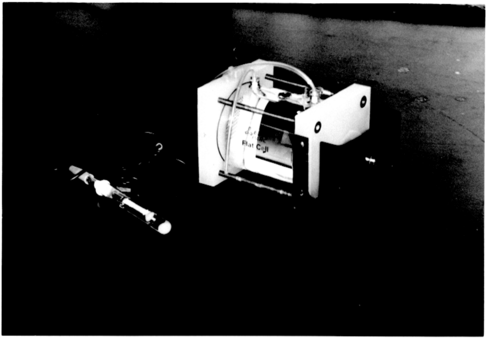

Figure 2: A photograph showing the polarization cell.
(a) reference electrode (SCE)

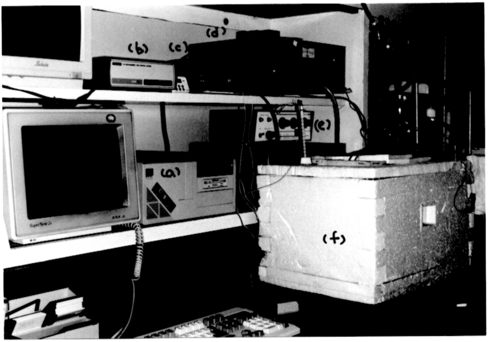

Figure 3: A photograph showing the equipment used in potentiodynamic scanning.
(a) microcomputer system, (b) Keithley 575 A/D controller,
(c) multimeter, (d) potentiostat/galvanostat, (e) temparature controller
(f) constant tempareture air bath.

Auxiliary electrode: A (6.25 +/- 0.05) cm^2 platinized titanium gauze was used as counter electrode. It was cleaned by soaking in concentrated hydrochloric acid and rinsing thoroughly with tap-water, distilled water, doubly distilled water and stored in doubly distilled water until ready for used.

Working electrodes: Commercial AISI 304 stainless steel and commercial UNS A91060 aluminium plates were used. Composition of the electrodes were tabulated in Table 9. (Appendix 1)[84].

Constant power supply: A Topward model TPS-2000 Series DC power supply from Topward Electric Instruments Co. Ltd. was used to control the applied current during electrolysis.

Digital voltmeter: A Simpson Model 461 digital multimeter was used to measure the applied potential across the electrodes.

Atomic absorption spectrophotometer: All atomic absorption measurements were made using a Thermo Jarrell Ash Corporation model Smith Hieftje 1000 Atomic Absorption Spectrophotometer.

Hollow cathode lamps: copper, chromium, iron hollow cathode lamps used were manufactured by Varian Techtron Pty. Ltd. Australia; and the nickel hollow cathode lamp used was manufactured by Photron Pty. Ltd. Australia.

A portable Witeg Model W100, two decimal (precision 0.01) combination glass electrode type digital pH meter was used to determine sample pH.

Micropipette: An Eppendorf micropipette, model Varipette 4710 range 1-100μl and 'Gilson pipetman' manufacture by Gilson Medical Electronics micropipette range 10-1000μl, and 10-5000μl were used in solution preparations.

Bubbling system: A President Aquarium air pump model EK-6000 was used to introduced air through a ceramic filter.

Polishing material: Commercial silicon carbide abrasive paper grain size 240 and 600 were used.

Image processing and analysis system: A Leica Image Processing and Analysis System model Q500MC was used to examine the precipitated hydroxide particles.

2.3 Solution Preparation

Nickel stock solution (20,000ppm): The solution was prepared by dissolving quantitatively 157.7120g hexahydrated nickel (II) sulfate and 19.5376g hexahydrated nickel (II) chloride with doubly distilled water in a 2 liter volumetric flask. The solution was diluted to the mark with doubly-distilled water. The nickel stock solution was stored in a 2.5 liter tinted glass bottle.

Copper stock solution (50,000ppm): The solution was prepared by dissolving quantitatively 268.28g dihydrated copper (II) chloride with doubly distilled water in a 2 liter volumetric flask. The solution was diluted to the mark with doubly-distilled water. The copper stock solution was stored in a 2.5 liter tinted glass bottle.

Chromium stock solution (50,000ppm)[18]*:* The solution was prepared by dissolving quantitatively 192.31g chromium (VI) trioxide with doubly distilled water in a 2 liter volumetric flask. 2 ml of concentrated sulfuric acid was added before the solution was diluted to the mark with doubly-distilled water. The chromium stock solution was stored in a 2.5 liter tinted glass bottle. Chromium would exist in the form of chromate and dichromate in the solution.

Stock solutions of 1.0 mol/L and 2.5 mol/L of NaCl were prepared by dissolving quantitatively 57.44g and 146.10g of sodium chloride with doubly distilled water in a one liter volumetric flask. The solution was diluted to the mark with doubly-distilled water.

5 mol/kg of NaOH stock solution was prepared by dissolving 80.00g sodium hydroxide with doubly distilled water in 400.00g of doubly-distilled water.

All solution storage bottles were stoppered and then sealed with teflon tape to prevent evaporation.

2.4 Electrochemical treatment of simulated effluent

Preparation of artificial heavy metal effluents: Artificial heavy metal effluents of different concentrations were prepare from nickel, copper, chromium stock solutions. Solutions containing varying (500, 100, 50 ppm) amounts of heavy metal ions in different concentration (0.01, 0.03, 0.05, 0.10 mol/L) of NaCl solutions were prepared. The actual heavy metal concentration prepared was further determined by atomic spectophotoscopy analysis.

Electrolytic cell: Photographs of the electrolysis cell material used and the cell setup are given in Fig (4) and Fig (5), respectively. 3 pairs of electrodes were placed in such the way that anode and cathode are adjacent to each other and (0.5 ± 0.1 cm) apart, separated and clamped together with plastic blocks as shown in the Figure 4. The cell was designed to be as simple as possible.

2.4.1 *Electrolysis process:*

The parameters being studied (as listed in Table 10. (Appendix 2)) are concentration of heavy metal, effect of NaCl concentration added, type of electrodes used, current density (from $2 mA/cm^2$ - $20 mA/cm^2$) and treatment time. The effect of agitation by using air bubbling and magnetic stirring were also considered.

Electrode preparation: Stainless steel and alumimium plates of 15 cm x 4 cm were used as materials for the electrodes. A fixed total surface area (7.0 ± 0.1)cm x (4.0 ± 0.1)cm for anode and cathode was obtained by masking off with synthetic polymer glue, and lacquer (W. Canning Materials Limited) the unrequired sections of the

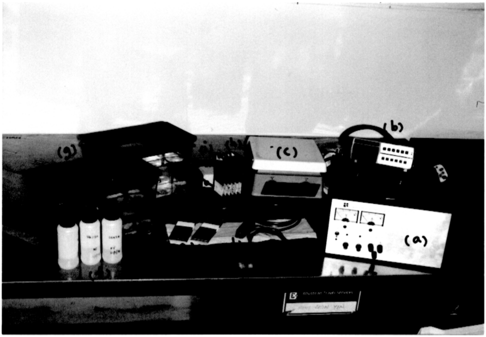

Figure 4: A photograph showing the equipment used in electrolysis process.
(a) constant power supply, (b) multimeter,(c) magnetic stirrer,
(d) & (i) air bubbling system, (e) aluminium anodes,
(f) plastic sample bottle, (g)electrolysis tank, (h) stainless steel electrodes.

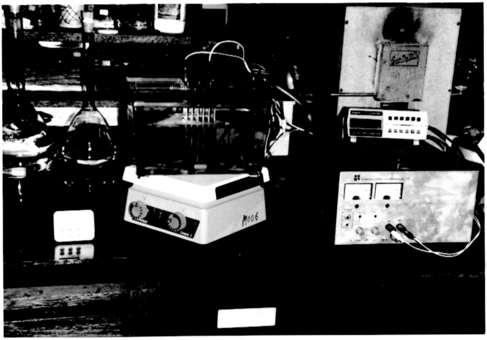

Figure 5: A photograph showing the setup of the electrolysis process.

electrodes. Each electrode was first coated with a thin layer of epoxy glue, and then with a few thin layers of lacquer. Each time it was left to dry first before the next layer was applied. The coated area was covered with paraffin ('NESCOFILM' sealing film) and followed by teflon film. The electrodes were rinsed with acetone, alcohol and doubly distilled water prior to used. 3 pieces of these electrodes were used as anode and cathode to give a total surface area of 168 cm^2. The total geometric electrode surface to solution ratio was 67.2 cm^2/L and all test results were based on this ratio.

The electrolysis was started once the electrodes were dipped into the bath which contained 2.5 liter of simulated effluent solution. The electrode pairs were placed in the middle of the electrolysis tank. Fixed (40ml) volumes of solution were pipetted out at intervals of 0, 15, 30, 45, 60, 90 minutes (some tests were conducted for longer periods (up to 420 minutes) for comparision), the total voltage across the system was also monitored. The collected samples were filtered through a 0.45μm cellulose nitrate 'Whatman' membrane filter, and then stored in plastic sample bottles for analysis (pH and atomic absorption analysis). All tests were carried out at ambient temperature. (27 ± 3 °C)

2.4.2 *pH measurement*: pH was measured using the Witeg pH meter, and using two-point calibrations with pH standards 4 and 7 [85]. Each pH reading reported was the average of several measurements (reproducibility +/- 0.05).

2.5. Atomic Absorption Spectrophotometry (AAS) for heavy metal determination

2.5.1. Toxic metals found in effluent from factories carrying out electroplating mainly include chromium, copper, nickel, zinc, cadmium, manganese and lead, of which the last three metals mentioned are generally present only in minute quantities in comparison with the other four. Analysis of the metallic contaminants has hitherto been carried out on the solution directly, before or after acidification with acid, to give values for the soluble amount of metals present in the effluents. In addition to the metals listed, other cations and anion such as iron and sulphate are often present, together with sodium salts arising from the treatment of the effluents before discharge. Atomic absorption methods have been applied to the determination of the toxic metals. Iron is reported to have a depressive effect on the absorption of chromium, but enhanced the absorption of nickel.[86-94] Belling[90] also reported that both sodium and chromium will interfere with nickel for such analysis. The used of strontium chloride in hydrochloric acid and ammonium salts[86-94] was shown to be effective in overcoming those effect. On the other hand, it has been reported that under proper conditions, this interference was negligible.[86-94]

2.5.2 *Analysis method*:

The analysis method was adapted from ASTM Standards Test Methods.[86]

Preparation of standard solutions: A series of 500, 250, 100, 80, 50, 30, 25, 20, 10, 8, 5, 2 ppm standard solutions were prepared by diluting the 1000 ppm standard solution in 50 or 100ml volumetric flasks. Doubly distilled water was used as blank.

Since the heavy metal content in the treated effluent samples varied from 500 ppm down to below 1 ppm, a less sensitive absorption wavelength was used to determined the approximate concentration before the used of the appropriate wavelength for each sample. Separate tests were made to check whether there were interference effects from NaCl and iron in the AAS analysis of the heavy metal ions under consideration. The effect of NaCl was checked by adding equivalent amounts of NaCl as used in electrolysis process (0.03, 0.05, 0.10 mole/L) to a known heavy metal standard solution. The iron interference was checked by the same procedure too.

It has been reported in the literature[87-93] that atomic absorption analysis of chromium should be carried out with Cr in either oxidation state 3+ or 6+. A series of solutions of known concentrations of mixed chromium 3+ and 6+ (by mixing known amounts of chromium (6+) stock solution with standard chromium (3+) solution) were tested.

By proper adjustment of the flame condition and with a suitable choice of wavelength, an analysis precision (+/- 5%) was obtainable and the results listed in Appendix 3 (Tables 11a-c) show that all the interference effects mentioned above can be considered negligible at this precision for the concentration ranges involved in this study. Comparison of results obtained for AAS determinations by diluting samples to the range of the most sensitive wavelength and by direct use of an alternate wavelength without diluting the sample shows little difference in the final results Appendix 4 (Tables 12a-c). Therefore, dilution of sample was applied only if a close alternate wavelength was not available. Some of the setting parameters were listed in Appendix 5.[93]

A random sample was chosen from time to time to check the reproducibility of the data obtained. All standards were freshly prepared for each series of analysis.

2.6 Chemical co-precepitation treatment method

Treatment procedure: A 500ml of simulated effluent solution (acidic) was used. A fixed amount (a few cm^3) of stock ferric chloride solution was pipetted into the solution. The solution was stirred by using a magnetic stirrer and solution pH was measured. A stock sodium hydroxide solution was slowly dropped into the solution to adjust the pH to between 6-9. 50ml of the solution was pipetted out, filtered through a 0.45μm cellulose nitrate 'Whatman' membrane filter, and then stored in a plastic sample bottle for further analysis. Ammonia solution was also used to raise the solution pH for some 500 ppm Cu samples. The test was carried out at ambient temperature. (27 ± 3 °C)

2.7 Potentiodynamic measurements

All potentiodynamic measurements were carried out in an air bath maintained at (25.0 ± 0.5 °C).

Working electrode preparation: The test stainless steel or aluminium plate was first polished with 240 and 600 (grain size) silicon carbide abrasive paper, and then washed with detergent and rinsed with doubly distilled water followed by acetone and alcohol to degrease the electrode surface. It was finally rinsed with doubly distilled water and air dried in a dust-free environment before use.

2.7.1 *Polarization process*

The anodic and cathodic polarization test method used was a modification of the ASTM G5-27 reference method[26,95]. The clean polarization cell was rinsed with the test solution before it was filled with it. After the electrodes were in place, the cell was connected to the scanning potentiostat and then left to equilibrate with the circuit open. When the measured open-circuit potential was steady to ± 5 mV for 10 minutes, actual measurement under computer control was commenced by running a program called IVSCAN15 written in Quick Basic (Appendix 6). The scanning potentiostat was used to control the potential sweeps. Automatic data acquisition was computer-controlled via a Keithley AD/DA controller. All data were store in ASCII format files on the hard disk of the computer system.

A reverse multiple scan method was applied, and the final steady-state I-E data were plotted as E vs. (log I) plots, where I is the current. Since A (surface area) = 1.0 cm^2, log (I/A) = log (j/Acm^{-2}), where j is the current density.

2.8. Heavy metal analysis

All quantitative analyses were carried out using atomic absorption spectrophotometry. To test qualitatively for the presence of iron and aluminium, the hydroxide precipitation method was applied. Based on the solubility product values[39-42] for these two metal hydroxide, if no hydroxide formed in the filtrate (electrolysis test samples) when sodium hydroxide was added (to adjust the solution pH to 9-10), it was ascertained that the ions contain in the solution was very low and well below the discharge limit (Appendix 7).[5]

2.9. Estimation of metal hydroxide particle size

The samples of wet precipitated ferric hydroxide were place between optical glass plates and observed using the image analyzer system. The images were captured and stored in a 486 based microcomputer system. Pd wire measured to be 26 μm using the Leica optical microscope was used to calibrate the image analyzer. The image analyzer consisted of a Leica image processing and analysis system microscope interfaced to the 486-microcomputer system via a Sony video camera attached to the Leica microscope.