RECOVERY OF GOLD FROM GOLD-COPPER AND GOLD-COBALT CYANIDE BASED ELECTROPLATING SOLUTIONS BY USING AN ELECTROGENERATIVE PROCESS

By

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A effective electrode surface area, m^2

A_s active electrode area per unit reactor volume, m^{-1}

A_e specific surface area, cm^2

C_0 initial metal concentration, mg L^{-1}

C_t metal concentration at time t, mg L^{-1}

E^0 standard reduction potential, V

k_m mass transport coefficient, m s^{-1}

R ratio

V_e cathode volume, m^3

V_R volume of electrolyte, m^3

V_1 overall cell potential, V

V_{1i} initial cell potential, V

V_{1f} final cell potential, V

V_2 cathode potential, V

V_{2i} initial cathode potential, V

V_{2f} final cathode potential

PEROLEHAN SEMULA LOGAM EMAS DARIPADA LARUTAN ELEKTRO-PENYADURAN EMAS-KUPRUM DAN EMAS-KOBALT SIANIDA DENGAN MENGGUNAKAN PROSES ELEKTROGENERATIF

ABSTRAK

Perolehan semula logam emas daripada larutan elektro-penyaduran emas-kuprum dan emas-kobalt sianida dengan menggunakan proses elektrogeneratif dijalankan dengan menggunakan sel statik. Katod yang digunakan dalam kajian ini ialah grafit berliang dan karbon kekaca berongga (RVC) sementara anod pula ialah kepingan zink. Kesan kehadiran logam kuprum dan kobalt terhadap pengendapan logam emas dikaji dengan menggunakan kaedah voltammetri. Kajian pemulihan logam emas dijalankan selama 6 jam dan kepekatan logam emas di dalam larutan dikaji dengan menggunakan spektroskopi penyerapan atom. Kajian permukaan dan ketulenan endapan logam emas pada elektrod dijalankan dengan menggunakan mikroskop elektron pengimbas yang dilengkapi spektroskopi penyebaran tenaga sinar-X (SEM-EDX). Hampir 99 % logam emas dapat diperolehi selepas 6 jam beroperasi dengan menggunakan katod yang permukaannya tidak diaktifkan dengan larutan palladium klorida. Hanya 3 jam diperlukan untuk memulihkan 99% logam emas apabila permukaan elektrod diaktifkan. Karbon kekaca berongga (RVC) yang telah diaktifkan permukaannya adalah bahan elektrod yang lebih baik berbanding grafit berliang, kepingan logam aloi dan kepingan kuprum. Lebih banyak logam emas dapat dipulihkan apabila permukaan elektrod yang lebih luas digunakan. Keputusan kajian juga menunjukkan bahawa larutan yang

mempunyai pH yang lebih tinggi daripada 10 dan mempunyai kepekatan sianida yang

tinggi dapat mengelakkan pengendapan logam kuprum bersama dengan logam emas.

ABSTRACT

The recovery of gold from gold-copper and gold-cobalt cyanide based electroplating solutions using an electrogenerative process was carried out with a batch cell. The cathodes that had been used for this studied were porous graphite and reticulated vitreous carbon (RVC) while for anode was zinc foil. The influence of the presence of copper and cobalt metal ions toward gold deposition was studied by cyclic voltammetry. The recovery studies were carried out for 6 hours during which the gold in the bath solutions was determined by atomic absorption spectroscopy at regular intervals. The surface morphology and purity of the deposited gold were determined using scanning electron microscopy – energy dispersive X-ray spectrometry (SEM-EDX). More than 99% of gold was recovered after 6 h of operation using non-activated cathodes. It takes 3 h to recover more than 99 % of gold using activated cathodes. Activated RVC is a superior cathode material having the highest recovery rate compared to activated porous graphite, stainless steel and copper sheet. More gold is recovered when using a greater electrode surface area that is exposed to the catholyte solution. The results also show that at pH greater than 10 and with higher free cyanide concentration, copper will not be co-deposited with the gold.

CHAPTER 1 INTRODUCTION

1.1 Gold

Gold is a precious soft yellow metal and is the most inert and noblest of the metallic elements. Gold has great stability, resistance to corrosion, high thermally, electrical conductivity, highest ductility and malleability of any metal (Reid and Goldie, 1974; Yannopoulos, 1991).

Gold is classified with copper and silver in group 1B of the periodic table, has a single s electron outside a completed d shell. Gold is very stable in air and in the majority of aqueous solutions, including strong acid. Gold only dissolves in oxidizing solutions containing certain complexing ligands such as cyanide, halides, thiourea and thiocyanate (Yannopoulos, 1991)

1.2 Gold Electroplating

Special properties of electrodeposited gold are high purity, high conductivity, low porosity and high corrosion resistance and also the ability to form excellent thermo-compression bonds and high reliability of the different types of connectors, printed circuits, relays and switches. Cyanide based gold formulations are very stable and always provide fine-grained gold deposits.

The first record of gold electroplating is in 1802 by Luigi V. Brugnatelli. In 1840 G. R. Elkington patented the forerunner of modern gold electroplating formulations based on the double salt gold potassium cyanide. From 1845, the process was commercially available for decorative gold electroplating. It was the growth of the electronics industry in the early 1940s that finally stimulated renewed interest in the science and technology of gold plating, since the electroplating become the major user of gold for the electronics industry (Reid and Goldie, 1974, Cui and Zhang, 2008).

Copper is a component of most gold alloys, it hardens the alloy and reduces its cost. Nickel is a component of many "white gold" alloys. Zinc is found in some gold alloys and in some solders used for gold alloys. Mercury is found in dental gold scrap. Lead and tin are components of a soft solder used for gold jewelry in fastening parts. Iron, steel and also brass wire are used as fine wires in holding parts of jewellery together while they are soldered (Reid and Goldie, 1974).

1.3 Fundamental Chemistry of Gold and Copper Recovery from Cyanide Solutions

When an aqueous solution of gold and copper is added to a solution containing cyanide ions, there will be some reaction. The following sections will discuss chemistry of gold recovery and the gold and copper ions reactions in cyanide solution with other catholyte and anolyte reactions.

1.3.1 The Chemistry of Gold Recovery in Electrogenerative Processes

The galvanic reactions in this electrogenerative process can be represented by the following equations (1.1) − (1.3) (Chi et al., 1997; Barbosa et al., 2001; Yap and Mohamed, 2007, 2008);

Anode: $Zn + 4CN^- \rightarrow Zn(CN)_4^{2-} + 2e^-$ $E^0 = 1.25$ V   (1.1)

Cathode: $Au(CN)_2^- + e^- \rightarrow Au + 2CN^-$ $E^0 = -0.60$ V   (1.2)

Overall: $Zn + 2Au(CN)_2^- \rightarrow Zn(CN)_4^{2-} + 2Au$ $E^0 = 0.65$ V   (1.3)
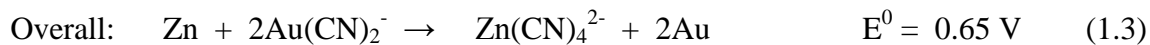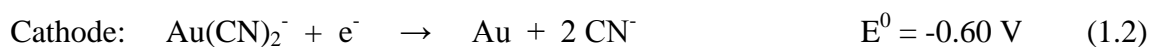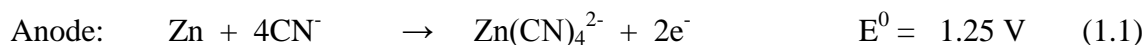
By combining equations (1.1) and (1.2), the overall process in the cell is given in equation (1.3).

1.3.2 The Chemistry of Cyanide Solutions

Sodium or potassium cyanide salts are quite soluble in water producing cyanide ions and metal cations. The cyanide ions will hydrolyze in water to form molecular hydrogen cyanide, which increase in pH according to equation (1.4) (Yannopoulos, 1991);

$CN^- + H_2O \rightleftharpoons HCN + OH^-$ (1.4)

Hydrogen cyanide is a weak acid (K_a = 4.89 x 10^{-10}) which dissociates in aqueous solutions according to equation (1.5) (Yannopoulos, 1991);

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^- \tag{1.5}$$

At pH 9.3, about half of the cyanide becomes free cyanide ions. As hydrogen cyanide has a relatively high vapor pressure, it readily volatilizes causing environmental problems and loss of cyanide. Consequently most of the experiments were carried out at pH greater than 10.

1.3.3 The Chemistry of Copper Ions in Cyanide Solutions

When an aqueous solution of Cu(II) is added into a cyanide solution, a brownish yellow precipitate will be formed and decomposes into cuprous cyanide and cyanogen gas according to the equation (1.6) (Longo and Buch, 1967);

$$Cu^{2+} + 2CN^- \rightarrow Cu(CN)_2 \rightarrow CuCN + \tfrac{1}{2}(CN)_2 \tag{1.6}$$
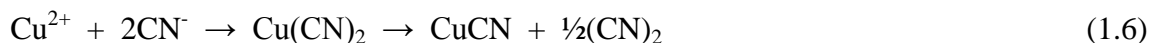
The cyanogen $(CN)_2$ species is then hydrolysed very quickly to more stable CNO^- ions in alkaline solutions. The other equilibrium of cuprous cyanide can be represented by equations (1.7) – (1.9) (Hsu and Tran, 1996; Lemos et al., 2006);

$$CuCN + CN^- \rightleftharpoons Cu(CN)_2^- \tag{1.7}$$

$$Cu(CN)_2^- + CN^- \rightleftharpoons Cu(CN)_3^{2-} \tag{1.8}$$

$$Cu(CN)_3^{2-} + CN^- \rightleftharpoons Cu(CN)_4^{3-} \tag{1.9}$$

1.3.4 The Chemistry of Gold Recovery from Cyanide Solutions

The gold reduction from alkaline solution is as shown in equation (1.10) – (1.12) (Mac Arthur, 1972);

$$Au(CN)_2^- \rightarrow [Au(CN)_2^-]_{ads} \tag{1.10}$$

$$[Au(CN)_2^-]_{ads} + e^- \rightarrow Au + 2CN^- \tag{1.11}$$

or

$$(AuCN)_2^- + e^- \rightarrow Au + 2CN^- \tag{1.12}$$

The gold reduction mechanism has two different reactions where one was through an adsorbed intermediate $(AuCN)_{ads}$ and the other is a direct charge transfer that will produce gold metal.

1.3.5 Cathodic and Anodic Reactions

Three main cathodic reactions are gold deposition (see equation 1.2), oxygen reduction and water reduction (Yannopoulos, 1991) as follows;

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \tag{1.13}$$

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \tag{1.14}$$

From a thermodynamic point of view, oxygen reduction is likely to occur first followed by gold deposition and water reduction. Thus, to remove the dissolve oxygen, the catholyte was deaerated with nitrogen gas before and during the experiments.

According to the reaction of gold deposition, the equilibrium potential for gold to deposit is strongly dependent on both cyanide ions and gold cyanide complex concentration.

There are two main anodic reactions and the most preferable reaction is the formation of zinc cyanide (equation 1.1) followed by cyanide oxidation;

$$CNO^- + H_2O + 2e^- \rightleftharpoons CN^- + 2OH^- \tag{1.15}$$

Zinc cyanide which had been produced is well contained and can be disposed by other methods of cyanide remediation. It can also be used as secondary raw material in the zinc plating industries (Yap and Mohamed, 2007).

1.4 Porous Graphite and Reticulated Vitreous Carbon (RVC) as Electrode Materials

Porous graphite and reticulated vitreous carbon (RVC) are both carbonaceous materials. Graphite is soft, has a hexagonal structure with the carbon atoms arranged in layer planes (see Figure 1.1). Porous graphite is a good electrical conductivity, high thermal conductivity, acceptable corrosion resistance, availability in high purity, dimensional and mechanical stability, light in weight and ease in handling, availability in a variety of physical structures, ease of fabrication into composite structures and low cost (Pierson, 1993).

Reticulated vitreous carbon, known as RVC combines some electrochemical properties of non-porous glassy carbon with some of normal industrial carbons. RVC is an open pore foam material, with a honeycomb structure. The material is available in several porosity grades from 10 to 100 pores per inches. RVC has an exceptional chemical inertness over a wide temperature range, high void volume (97%), high surface area combined with self-supporting rigidly, low resistance to fluid flow and electrical conductivity. RVC had been used for several non-electrochemical applications, including filtration, high temperature insulation (heating
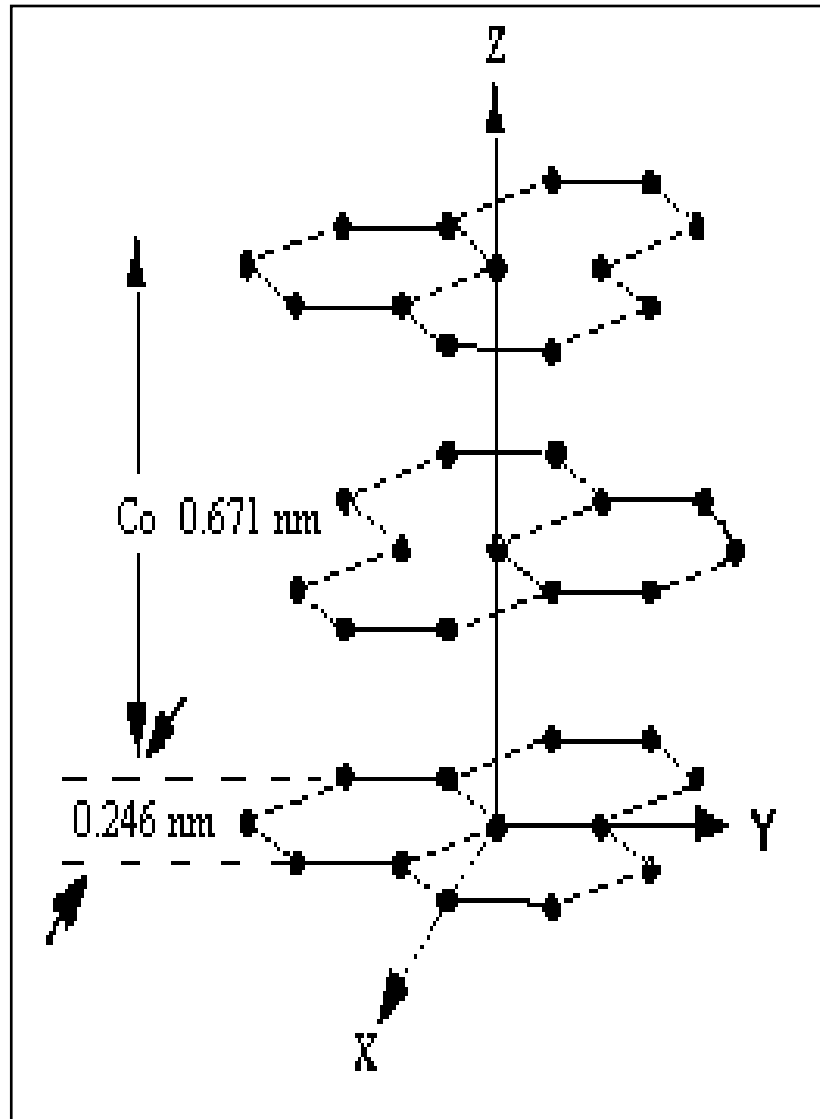
Figure 1.1 Graphite crystal structure (Pierson, 1993)

element in various appliances), acoustical control and others (Wang, 1981; Friedrich *et al*., 2004).

Due to its special structure, physical, chemical and electrochemical characteristics, RVC has become an extremely attractive material for various electrochemical purposes such as a porous electrode for the detection of electroactive species in flowing streams (liquid chromatography), for electroorganic synthesis, for the removal of metal ions from waste streams and for various other industrial electrolytic processes. RVC has been widely used in removal or recovery of metal ions because of the advantages of high void volume and large pore dimension, resulting with sufficient porosity (minimum resistance to flow) even after deposition of a thick metal film (Wang, 1981; Friedrich *et al*., 2004).

1.5 Introduction to Electrogenerative Processes

An electrogenerative process is a process which does not require any external electricity supply for the recovery of precious metals. An electrogenerative process which is also known as galvanic cementation is a galvanic process. The system has the ability to recover metals without any external supply of energy due to the spontaneous electrochemical reaction that occurs. The electrogenerative process can be made selective for particular reactions by varying the electrode potential and using suitable electrodes.

The electrogenerative process has been used for recovery or removal of metal ion from solution, selective electrosynthesis of chemicals and leaching of sulfide minerals where the electrochemical routes can replace the production of toxic intermediates and hazardous process conditions.

Over the past three decades, the electrogenerative system has been investigated by various scientists such as Kumar and Vasu (1972), Langer and Anderson (1976), Prakash et al. (1978), Illangovan and Vasu (1980a,b) Sedahmed and Fawzy (1985), Tran and Langer (1993), Dieckmann and Langer (1997, 1998) , Hor and Mohamed (2003, 2005) and Yap and Mohamed (2007, 2008). This system has successfully recovered copper from wastewater (Hor and Mohamed, 2003, 2005), gold from simulated gold cyanide solution (Yap and Mohamed, 2007, 2008) and also reduction of hexavalent chromium to trivalent chromium (Abdo and Sedahmed, 1998).

1.6 Objective of Study

The main objective of this study is to recover gold from gold-copper and gold-cobalt spent electroplating bath solutions using an electrogenerative system. The electrogenerative system had been proven as a successful technique to recover gold by Wan Ngah (1996) and Yap and Mohamed (2007, 2008). An improvement has been made to the cell design used by Wan Ngah (1996) which has resulted in higher gold recoveries.

Studies by Wan Ngah (1996) and Yap and Mohamed (2007, 2008) were focused on recovery of gold from gold cyanide solutions. Wan Ngah (1996) had achieved more than 90 % gold recoveries in 8 hours. Yap and Mohamed (2007, 2008) had concluded that gold can be recovered more than 99% from gold cyanide solutions. This study will be focused more on recovery of gold from gold-copper and gold-cobalt electroplating solutions by using an electrogenerative process in terms of optimum conditions for maximum gold recovery and the purity of the gold deposited.

First, cyclic voltammetry studies were carried out to determine the potential range at which the selective deposition of gold can be carried out in the presence of a high copper, cobalt and cyanide concentrations. Then, the recovery of gold using two different static batch cells was investigated. The difference between these two cells is the electrode surface that is immersed in solution. The parameters that will be studied with respect to the percentage of gold recovered are cell design, Pd/Sn activation of the cathode surface by a modified Shipley solution, catholyte pH for selective gold recovery and various cathode materials. Finally, the characterization of gold deposits on electrode materials was studied by using scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDX).

CHAPTER 2 LITERATURE REVIEW

2.1 Recovery of Precious Metals

Over the past years, almost every electroplating and metal finishing operation has installed wastewater treatment systems in order to remove contaminants so that the effluent meets government environmental standards. The high cost for disposal of wastewater contaminants and the public pressure on industry to reduce toxic chemical emissions into the environment has caused the electroplaters and metal finishers to respond to this challenge by seriously evaluating and implementing recycling and recovery techniques.

Varieties of methods are found in the literature to recover precious metals from different solutions. There are several methods available for the recovery and removal for precious metals from solutions. These methods include cementation, solvent extraction, adsorption on activated carbon, ion exchange and electrowinning.

2.1.1 Cementation or Precipitation

Cementation or precipitation is the oldest hydrometallurgy technique for recovering metals in elemental states from aqueous solutions. Cementation or precipitation with zinc has been in used for a long time to recover gold and silver from

cyanide solutions in larger scales. Other than zinc, aluminium and magnesium are other metals to find limited use in the cementation or precipitation of these precious metals.

There are four important reactions when zinc metal is brought into contact with gold or silver cyanide solution, which are zinc dissolution, gold or silver precipitation, hydrogen evolution and consequent increase of alkalinity of the solution. These reactions can be well explained based on the following equations that take place during zinc cementation (Gupta and Mukherjee, 1990):

$$KAu(CN)_2 + 2\ KCN + Zn + H_2O \rightleftharpoons K_2Zn(CN)_4 + Au + \tfrac{1}{2}H_2 + KOH \qquad (2.1)$$

$$Zn + 4KCN + 2H_2O \rightleftharpoons K_2Zn(CN)_4 + 2KOH + H_2 \qquad (2.2)$$
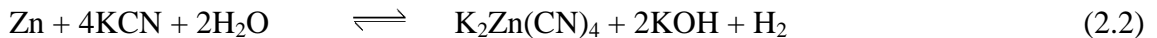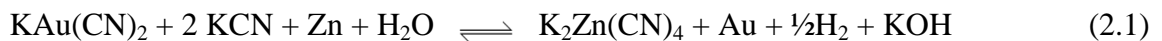
In order to achieve the completion of the zinc cementation reaction, the effluent should contain sufficient free cyanide concentration. Higher free cyanide concentration can lead to the excessive consumption of zinc. In practice, if the cyanide concentration is reduced too much, a passivating layer of zinc hydroxide may form on the surface of zinc particle. The cementation of gold is practically run in constant pH range 8-11. The dissolved oxygen also has to be first removed as it can cause back dissolution of the precious metal. However, gold cementation can produce impurities of product with the co-deposition of other metals such as lead, copper, nickel, arsenic or antimony (Fleming, 1992; Hsu and Tran, 1996). Cementation of gold and silver can be carried out either in Zn boxes or in a Merrill-Crowe equipment system. Precipitant in boxes is an older and

less efficient technique compared to Merrill-Crowe process (Gupta and Mukherjee, 1990).

The Merrill-Crowe process is a separation technique for removing gold from cyanide solution. The solution is separated from the ore by methods such as filtration and counter current decantation (CCD) and then the gold is cemented by adding zinc dust, which precipitate the gold. The zinc has higher affinity for the cyanide ion than gold. The precipitate is further refined, by smelting to remove the zinc.

The Merrill-Crowe process, originally patented by Salman and Pichard, was applied in 1897 to the Homestake operation in Lead, South Dakota by C.W. Merrill. In 1916, the process was refined with T.B. Crowe's vacuum deaerator which causes an improvement in the system efficiency. Since then, the Merrill-Crowe process has been commercially use in the precipitation of precious metals from cyanide solution (Chi *et al*., 1997). The flow chart of the Merrill-Crowe process is shown in Figure 2.1.

The disadvantages of the cementation process are that other metal ions will be precipitated as well and thus accompanying systems are needed for recycling (Grosse *et. al.*, 2003).
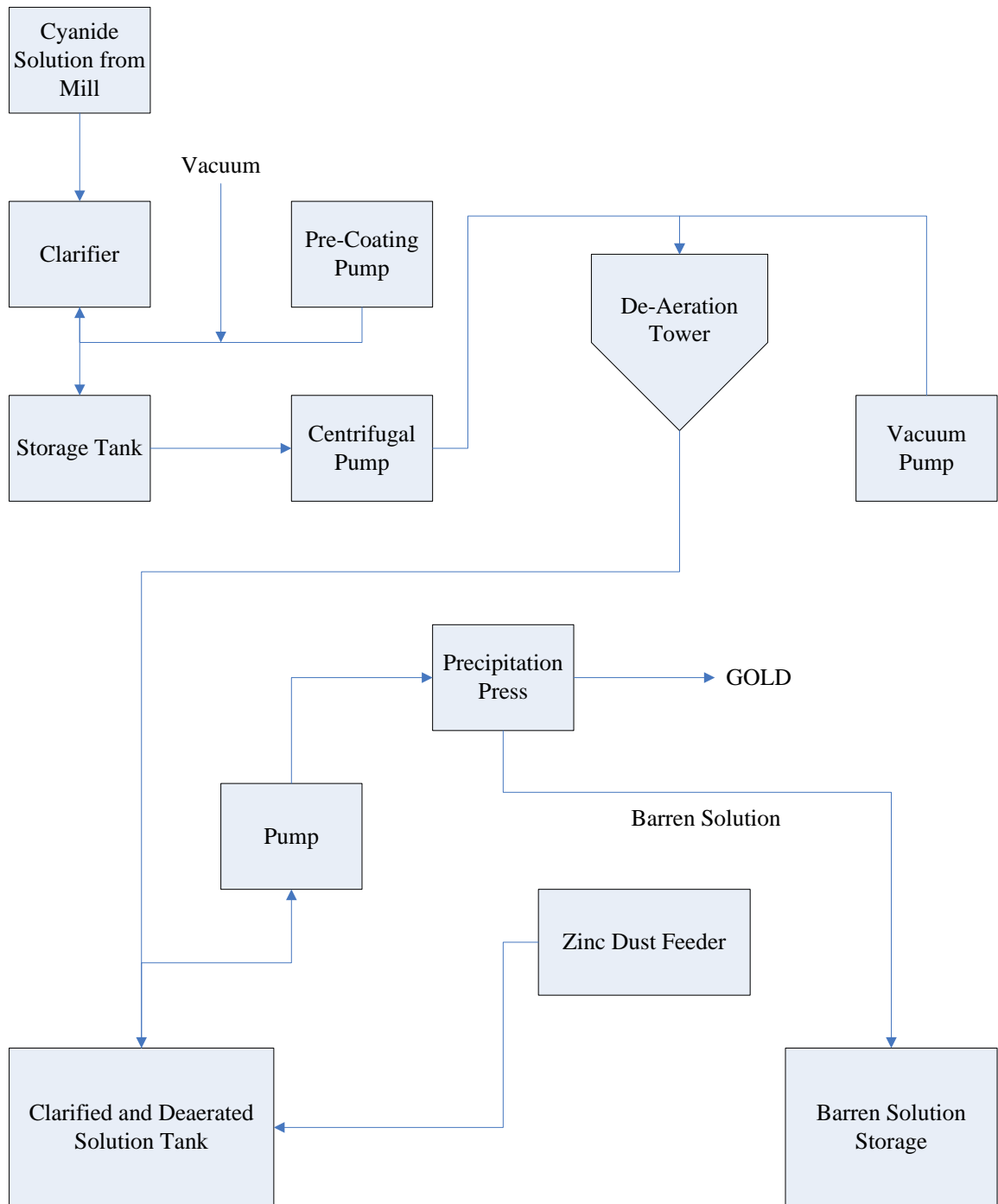
Figure 2.1 Merrill-Crowe gold precipitation processes (Gupta and Mukherjee, 1990).

2.1.2 Solvent Extraction

Most of the research work has been concentrated on the application of alkyl amines and quaternary ammonium salts, which extract gold from cyanide solutions as the dicyanoaurous ion:

$$R_4NX_{(org)} + Au(CN)_2^- \rightleftharpoons R_4NAu(CN)_{2(org)} + X^- \qquad (2.3)$$
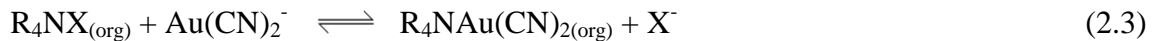
where R is given as a hydrocarbon chain or hydrogen atoms and X is an organic anion, such as chloride (Monhemius, 1994).

In general, the extraction of $Au(CN)_2^-$ by tertiary and lower aliphatic amines under acidic conditions is not suitable for use with gold cyanide leach liquors, which always have more alkaline pH. However the use of organic phosphorous oxides as organic phase modifiers change the pH of the amines and enable gold to be extracted at the natural pH of the leach liquors (Mooiman and Miller, 1984). Then, Mooiman and Miller (1991) later reported that phosphorus organic compounds, tributyl phosphate (TBH) and dibutyl butyl phosphate (DBBP) could extract gold from cyanide solutions by a solvation mechanism.

The quaternary ammonium salts for the extraction of gold from cyanide solutions has countered some problems, mainly because of the formation of emulsions between the organic phase and the cyanide solutions. Riveros (1990) has reported that this problem can be overcome by proper choice of diluents. The Solvesso 150, fully aromatic

diluents were found to be better than the usual aliphatic diluent because it can eliminate emulsification with the quaternary ammonium extraction, Aliquat 336 (tri-(C_8-C_{10}) alkyl methyl ammonium chloride). High loadings of gold in the organic phase (2-3 g Au/L) could be achieved from leach liquors containing 10 mg L^{-1} Au (I) when an experiment of small continuous circuit was run.

The disadvantages of this technique are solvent extraction produces organic waste. There will be an increase in operating costs because of the need to produce clarified liquor and the need for an accompanying system for recycling purposes (Grosse *et. al.*, 2003).

2.1.3 Adsorption on Activated Carbon

In the treatment of gold ores, activated carbon is used in carbon-in-pulp, carbon-in-leach and carbon-in-column processes. In each case carbon adsorbs gold complexes present at low concentrations (2 mg L^{-1}) in slurries or pregnant solutions. The efficiency of these processes directly influences the gold recovery yield and consequently the profitability of the gold mining operation. Most of the development and optimization work in gold cyanidation plants with carbon have been done empirically. Metallurgist, chemists and activated carbon manufacturers have put much effort into increasing the basic understanding of the activated carbon process efficiency. The adsorption mechanism in particular has been given detailed attention. Apparently, a consistent

picture of what is occurring on a molecular scale has emerged (McDougall *et al.*, 1980; Bansal and Goyal, 2005).

Activated carbon is a highly porous solid produced by the carbonization reaction under controlled conditions. Performance of the product depends on the conditions of carbonization and the type of raw material used. The characteristics and specifications of activated carbon vary widely and are dependent upon the raw material used for the activated carbon production. Although many characteristics exist, some are more significant than others. Activated carbon specifications/characteristics that should be considered, reviewed and understood for the recovery of gold from cyanidation processes are pore volume, pH (of water extract), bulk density, total surface area, pore radius/volume distribution, average pore radius, mesh size and attrition resistance (McDougall *et al.*, 1980; Bansal and Goyal, 2005).

The best use of activated carbon in processes for the recovery and purification of gold and silver, not only with respect to the adsorption and elution of these metals on carbon, but also in relation to the effective activation and regeneration of the carbon for repeated use, can be obtained only with a good knowledge of the mechanism that govern the adsorption of the various metal cyanide complexes on carbon and of the factors that influence their adsorption. In spite of the importance of the process, no consensus has been reached regarding the mechanism by which species are adsorbed on activated carbon. The carbon sizes from as coarse as 6-mesh to as fine as 28-mesh have proved to be effective in practice depending on Carbon-in-Leach (CIL), Carbon-in-Pulp (CIP) and

Carbon-in-Column (CIC) (McDougall *et al.*, 1980; Bansal and Goyal, 2005). The process flow chart for the recovery of gold by activated carbon is shown in Figure 2.2.

The disadvantage of adsorption or activated carbon is the gold complex produced is not in a metal form (Grosse *et. al.*, 2003).

2.1.4 Ion Exchange

The use of resins to extract gold from cyanide solution started as early as 1961 in South Africa. Ion exchange resins then have been widely used in wastewater and water treatment processes, including at drinking water treatment plants as a purification process. Ion Exchange is the process of purifying a liquid solution by passing it through a bed of ion exchange resins. An exchange of ions between the liquid and the solid ion exchange resin takes place and is controlled by the functional group attached to the resin matrix. Cation resins have a negative fixed charge and exchange the positively charged ions; anion resins have a positive fixed charge and exchange the negatively charged ions. The exchange of ions is reversible in most instances by passing a highly concentrated regenerator solution through the bed of ion exchange resin (Fleming and Cromberge, 1984; Gomes *et al*., 2001).

Anion exchange resins have a high selectivity for the anionic gold complexes usually encountered in gold cyanidation plants. Gold cyanide is most commonly found in mining and plating waste but waste streams containing gold chloride are not known.
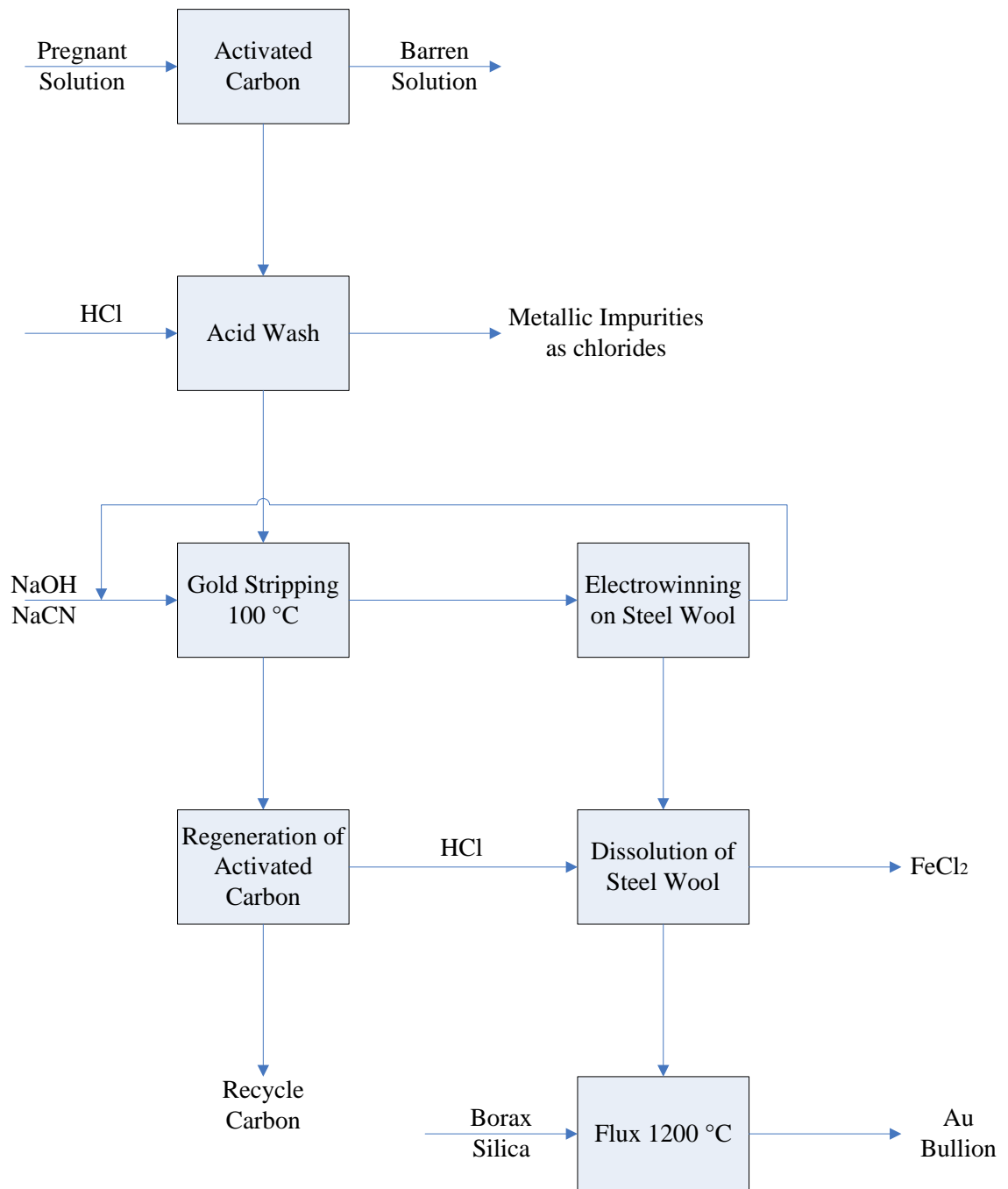
Figure 2.2 Recovery of gold by activated carbon process (Bansal and Goyal, 2005).

Owing to the high affinity of anion exchange resins for gold containing anions, the main problem is to recover gold from resin rather than recovery of the aurocyanide ion from the stream (Fleming and Cromberge, 1984; Gomes *et al*., 2001).

Gomes *et al*. (2001) used three different resins (one cationic, two anionic) for gold recovery process from solutions containing anionic cyanide complex $Au(CN)_2^-$. They reported that the strong base anionic resin, Purolite A-400, regenerated with a 5 % (wt) NaCl is more efficient in terms of gold recovery than the regeneration with 4 % (wt) NaOH. The weak base anionic resin, Purolite A-100, regenerated with a 4 % (wt) NaOH was selected for further experiments of gold recovery from low concentration cyanide solutions due to the fact that the weak resins are easier to elute than strong resins, enabling an easier recovery of the removed solute and moreover, the strong resins, regenerated with NaCl, would probably release chloride ions to the effluent.

The disadvantages of ion exchange technique are it is difficult to find a suitable resin for solutions containing mixtures of metal ions. The resin is sensitive to temperature and expensive. Moreover this technique needed accompanying systems for recycling (Grosse *et. al.*, 2003).

2.1.5 Electrowinning or Electrolytic

Gold can be recovered from solutions by electrolysis, a process that is known in the extractive metallurgy industry as electrowinning. When two electrodes (cathode and

anode) are placed in a solution containing metal ions and an electric current is passed between them, the metal can be deposited on the negative electrode. In the recovery of most metals, oxygen is evolved from water at the positive electrode. An electrolyte and a current density is generally chosen so as to give dense, compact electrodeposits, and some additives could be included in the electrolyte to further improve product quality.

There are various workers dealing with the electrowinning of gold, either from mining industries or electroplating wastes (Stavart *et al*., 1999; Barbosa *et al*., 2001; Reyes-Cruz *et al*., 2002, 2004; Spitzer and Bertazzoli, 2004). Stavart *et al*. (1999) used carbon felt as electrode material in a three-dimensional cell (Microflow Cell provided by Electrocell AB) and successfully reduced gold concentration from 30 mg L^{-1} to 2 mg L^{-1} (93%) with current efficiencies ranging from 6% to 12% being achieved.

Barbosa *et al*. (2001) used a modified Zadra cell with two different kinds of cathodes, mild steel wool (MSW) and a stainless steel mesh coil (SSM). They have reported that SSM was a better cathode material compared to MSW in terms of gold recovery because of the surface area distribution and homogeneity, which allows a better flow of the electrolytic solution through it, avoiding the bypass of electrolyte. Gold can be recovered up to 99.8% with SSM as cathode in 60 minutes. They also reported that the selectivity of gold recovery can be achieved with suitable cathode potential and pH of the gold cyanide solution has a strong influence in the electrolyte conductivity.

Reyes-Cruz *et al*. (2004) have reported recoveries of 26% of gold and 48% of silver by using a three-dimensional electrochemical reactor (FM01-LC) with a RVC

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electrode. Spitzer and Bertazzoli (2004) used a filter-press type electrochemical reactor and recovered 67% to 90% of gold, 90% to 95% of silver and 10% to 20% of copper with current efficiencies ranging from 15% to 23%.

The disadvantage of electrowinning or electrolytic technique is it need power consumption. When dealing with low concentration of precious metal ions, such reaction as oxygen and water reduction will occur which cause low current efficiencies in the systems (Grosse *et. al.*, 2003).

CHAPTER 3 EXPERIMENTAL

3.1 Chemicals

A listing of chemicals that were used in this study is given in Appendix A.

3.2 Equipment and Apparatus

3.2.1 Batch Cell

The schematic diagram of the batch cell is shown in Fig.3.1. The cell, with two compartments for the cathode and anode, was made of Plexiglas. Copper sheets were used as current collectors and were attached to the electrode. The current collectors were connected by an external conducting wire to complete the circuit. The output current and potential of the system were measured by two multimeters. A saturated calomel electrode (SCE) with a luggin capillary was used as a reference electrode. The two compartments were separated by a cation exchange membrane. The two compartments were joined together using ten nuts and bolts.

Figure 3.1(a) shows a schematic diagram of Cell 1 used by Wan Ngah (1996) with two electrolyte compartments of dimensions 4 cm x 4 cm x 6.5 cm. Figure 3.1(b) shows a schematic diagram of a modified cell (Cell 2) with dimensions 4.5 cm x 5 cm x

5 cm. The difference between the two cells is the electrode surface area that is in contact with the electrolyte. For Cell 1, the cathode surface area in contact with the electrolyte is 2 cm x 2 cm x 0.2 cm and for Cell 2, the electrode surface area is 2 cm x 4.5 cm x 0.2 cm.

3.2.2 Others Equipment and Apparatus

Two types of multimeters which were used to measure the output current and potential of the system were Fluke 77 Series II multimeter and Fluke RMS 189 multimeter respectively.

A saturated calomel electrode (SCE) supplied by Hanna Instruments was used as the reference electrode. The reference electrode was needed for cathode potential measurement in the batch cell.

The pH was measured by using pH meter model is Delta 320 with LE438 pH electrode which was supplied by Mettler Toledo.

The conductivity meter model is CP-4303 and was supplied by Lutron Electronic Enterprise Co. Ltd.

Cyclic voltammetric studies were performed using an eDAQ EA 161 potentiostat connected to an e-corder unit with EChem software.