Electrochemical Recovery of Gold from Waste Electric and Electronic Equipment Using Circulating Particulate Bed Reactor (CPBE)

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Abstract. The utilization of electrochemical process recovery involving low reactant concentrations of metal requires electrodes with high mass transport rates and specific surface areas. This is essential to increase cross-sectional current densities whilst optimizing the capital and operating costs. Experimental results demonstrated that Circulating Particulate Bed Reactor (CPBE) is suitable for the recovery of low concentrations of gold from aqueous chloride solution containing AuCl₄⁻ and AuCl₇⁻ of less than 0.5 mol m⁻³(< 10² g m⁻³). Elemental gold was successfully obtained on 0.5-1 mm gr particles in an electrochemical reactor incorporating a cation-permeable membrane and operated in bath recycle mode. Depletion to concentration < 5 x 10⁻³ mol m⁻³ (< 1 g m⁻³) appeared to be mass transport controlled at an applied potential of +0.20 V (SCE), specific electrical energy consumption (SEEC) of ca. 800-1300 kWh h (tonne Au)⁻¹ for cell voltages (U) of 2.0-3.0 V, and fractional current efficiencies of ca. 0.95. However, atomic absorption and UV spectrophotometry established that as the ([AuCl₄⁻] + [AuCl₇⁻]) concentration decayed, the [AuCl₄⁻]/[AuCl₇⁻] molar ratio changed. A multi-step mechanism for reduction of AuCl₄⁻ ions explained this behavior in terms of changing overpotentials for AuCl₄⁻ and AuCl₇⁻ reduction as total dissolved gold concentration decreased. In addition, SEM images confirmed that adherent and coherent Au deposits were achieved with CPBE for Au deposition under mass transport control at 0.20 V (SCE).

1. Introduction
The production of electrical and electronic equipment (EEE) is known as one of the fastest growing businesses in the world [1]. New applications of EEE are increasing significantly at the same time as the average replacement process accelerating. The rapid development has resulted in an increase of end of life or waste electric and electronic equipment (WEEE), which can be a valuable source of secondary raw materials if treated appropriately [2].

Technologies that are able to combine metal removal with metal recovery are becoming increasingly important. This is because they are able to convert wastes from an economic liability to a saleable resource, which results in the production of little or no waste, and simultaneously protects the environment.

Current recycling processes are mainly pyrometallurgical, the WEEE being smelted at high temperature which consists of the thermal treatment of minerals and metallurgical ores and concentrates to bring about physical and chemical transformations in the materials to enable recovery of valuable metals [2]. The cost effectiveness of pyrolytic recycling for WEEE, apart from those with relatively high precious metal content, coupled with increasing ecological concerns has cast doubt...
over the long-term viability of this methodology and has provided impetus for the development of more sustainable approaches embracing mechanical and hydrometallurgical technologies. Although majority of metals can be recovered by pyrometallurgical processes, the organic yields are combusted and subsequently produce noxious gasses that are harmful to the environment [3]. Hydrometallurgical processes allow a more environmentally benign and energy efficient route which requires two stages of process to metal reclamation from shredded WEEE; metal dissolution into an aqueous media and followed by recovery of metal ions.

A number of papers [4-8], including a more recent one [9], have been written on the electrodeposition of gold particularly from chloride complexes. However, in each case, it is from a solution at different concentration several orders of magnitude greater than would be expected from gold concentration in WEEE leachate which was around 0.05 mol dm$^{-3}$. Nicol [5] have studied the gold electrodeposition in acidic chloride media and found gold deposition to be mass transport controlled and the limiting current proportional to the Au$^{III}$ concentration. Nonetheless, they were able to detect Au$^{I}$ intermediates by oxidation at a Pt ring electrode. Harrison and Thomson [6] also studied gold electrodeposition from chloride electrolytes using rotating disc electrode but unfortunately neglected the presence of Au$^{I}$ species. Diaz [8] studied the effects of Au$^{I}$: Au$^{II}$ molar ratio, pH and Cl$^{-}$ concentration on the voltammetric behavior of a Pt electrode to enable the kinetics and mechanism of gold dissolution and deposition to be determined. According to their investigations, at $+0.80$ V (SCE), Au dissolved exclusively as AuCl$_2$ ions, the proportions of AuCl$_4$ ions increasing at higher potentials.

Removing gold from chloride solution specifically produced from WEEE was further investigated by Cheng [9] using a packed bed cathode operated in batch recycle mode with a stirred tank reservoir. The packed bed cathode of 2-3 mm graphite particles was able to deplete ([AuCl$_4$] + [AuCl$_2$]) in 1 kmol m$^{-3}$ aqueous HCl from 0.5 mol m$^{-3}$ (10$^2$ g m$^{-3}$) to < 5 x 10 mol m$^{-3}$ (<1 g m$^{-3}$), essentially under mass transport control, with current efficiencies of $<$4F (mol Au)$^{-1}$. The investigation established that as the [AuCl$_4$]:[AuCl$_2$] molar ratio decayed from an initial value of ca. 0.3 to < 0.05 over the first ca. 500s which then increased passing through a maximum after 500-1500 s depending on the flow rate. In addition, a multi-step mechanism for reduction of AuCl$_4$ ions involving adsorbed Au$^{II}$ and Au$^{I}$ species was proposed to explain this behavior in terms of changing overpotentials for AuCl$_4$ and AuCl$_2$ reduction as the total dissolved gold concentration decreased and changing [AuCl$_2$]: [AuCl$_4$] molar ratios.

For a low concentration of metal ion in waste electronics such as gold, platinum and palladium, a three-dimensional cathode, with a high surface area per unit volume and high mass rate coefficients, is the best option to be used for metal recovery. Since the concentrations of gold in leachate solutions from WEEE are likely to be below 1 mol m$^{-3}$, a CPBE reactor is attractive for the deposition of gold. In this paper, the cathode potential, charge yields, specific electrical energy consumptions, and deposit morphologies of gold electrodeposition in CPBE will be determined.

2. Procedure

2.1. Experimental Setup

Figure 1 shows arrangement of the components in an individual unit cell, each contained by a Perspex frame (240 mm (h) x 145 mm (w)x 50 mm (t)), separated by a 2 mm thick rubber gasket to prevent short circuit by contacts between cathode, membrane and anode, while allowing electrolyte, and hence ionic current, to pass through. The electrolyte flowed from the bottom to the top of reactor and even distribution of the electrolyte. The unit cell were compressed together by two stainless steel plates on each side of the frame to ensure good electrical contacts between the Ti-feeder cathode and the graphite particles electrodes. The anode was a mesh Ti/Ta$_2$O$_5$-IrO$_2$ while the particulates bed cathode consisted of 40 cm$^3$ of graphite particles with an averaged diameter of 0.5-1.0 mm and a total surface area of c.a. 0.2 m$^2$.

The applied feeder cathode potential was controlled with respect to a saturated calomel reference electrode (SCE) by a computer-controlled AUTOLAB PGSTAT30 potentiostat/galvanostat (coupled with a 10A current booster), which also measured the current through the reactor. The catholyte and
anolyte compartment were separated by a Nafion-N424 membrane to prevent partially reduced metals ions from the cathode transferred to the anode, re-oxidised subsequently and reducing charge efficiency. The catholyte was 4 kmol m$^{-3}$ HCl + 1 kmol m$^{-3}$ NaCl solutions containing 0.5 mol AuCl$_4^-$ m$^{-3}$ and the anolyte was 1 kmol m$^{-3}$ H$_2$SO$_4$. Both catholyte and anolyte were operating in batch recycle mode with separate reservoirs. The catholyte flow rate was measured by a flow meter (Omega FTB603) and logged by data acquisition device (NI DAQPd-6015, National Instruments) and software (LabView™).

The reason for the flow of the anolyte was to aid the removal of gas bubbles evolved from the anode, since build-up of bubbles would reduce the effective conductivity of the anolyte and increase the cell voltage. A schematic of the flow circuit is shown below. The piping arrangement used was George Fischer PVDF piping. Two 12 V DC Totton pumps were used to pump the fluids from their reservoirs through the anode and cathode chambers and back to the reservoirs again. Two 10 L glass reservoirs were used as catholyte and anolyte reservoirs. The schematic diagram of electrochemical reactor flow circuit is shown in figure 2.

2.2 Characteristics of samples

Samples of catholyte were taken from the reservoir at fixed time intervals. Each sample was diluted at a ratio of 1:50 in 0.5 M HCl before metal ions concentration was analyzed by ICP (Inductively Coupled Plasma – Perkin Elmer Instruments Optical Emission Spectrometer Model Optima 2000 DV). In addition, the morphology of metal deposits on pre-metallised graphite particulates obtained under different potentials had been studied using SEM (Scanning Electrons Microscopy, SEM – JEOL 5610). The effects of applied feeder cathode potential and electrolyte flow rate on the Cu recovery rates and charge efficiency had also been investigated.

![Figure 1. Arrangements of components in a cell](image-url)
Figure 2. Schematic diagram of the experimental setup of the circulating particulate bed cathode electrochemical reactor (CPBE).

3. Results and discussion
3.1 Electrode potential analyses
Figure 3 shows the results of the negative-going linear potential sweep from +0.60 V (SCE) to 0 V (SCE) for the reduction of AuCl\textsuperscript{4-} ions in the CPBE reactor, at a flow rate of 0.25 dm\textsuperscript{3} min\textsuperscript{-1}. The current was noisier than for a planar rotating disc, due to the small potential drop in the 3D electrode and the noise due to the variation in number of particles in contact with the feeder at any time. However, it was possible to see that the reduction of gold is mass transport controlled at +0.20 V (SCE). The mass transport controlled current when the particles were circulating, was about half the initial current with no flow, suggesting that about 50% of the particles were active at any one time. While it would have been possible to deposit gold as a packed bed, if the particles were not moving, there was the risk of forming bridging deposits and poor deposit morphologies. With no flow to replenish reactants, the gold would also have been depleted and the reaction rate would have decreased quickly in a packed bed reactor, and so overall the gold deposition rate was unlikely to be faster for the CPBE reactor. The reactions that take place at the cathode are as follows:

\[ \text{AuCl}_{2}^{+} + e^{-} \rightleftharpoons \text{Au} + 2\text{Cl}^{-} \quad (1) \]

\[ E_{\text{AuCl}_{2}^{+}/\text{Au}(\text{SHE})}/V = 1.152 + 0.0296 \log(\text{AuCl}_{2}^{+}) - 0.118 \log(\text{Cl}^{-}) \quad (2) \]

\[ \text{AuCl}_{4}^{-} + 3e^{-} \rightleftharpoons \text{Au} + 4\text{Cl}^{-} \quad (3) \]

\[ E_{\text{AuCl}_{4}^{-}/\text{Au}(\text{SHE})}/V = 1.0006 + 0.0197 \log(\text{AuCl}_{4}^{-}) - 0.0789 \log(\text{Cl}^{-}) \quad (4) \]
During the electrodeposition process of gold onto the unseeded graphite particles, the AuIII concentration was calculated from the solution absorption, measured by UV-Vis spectrophotometry through fibre optics apparatus, using the absorptivity for AuIII concentrations (λmax = 312 nm, molar absorptivity, ε312 = 662.1 mol−1 m−1), so enabling AuIII / AuI molar ratios to be determined. The total of gold concentration of each sample was also analyzed using ICP (Inductively Coupled Plasma – Perkin Elmer Instruments Optical Emission Spectrometer Model Optima 2000 DV). Figure 4 depicts the reading of the absorbance of solution during gold electrodeposition in CPBE for ca. 3 hours. The peak at ca. 225 nm was contributed by the concentration of aqueous chlorine in the sample.

As can be seen, figure 5, and as was expected from the kinetic measurements at the planar RDE, the reduction of AuCl4− ions was faster than that of AuCl2− ions on carbon due to the additional overpotential driving force required for the nucleation of a new phase. This resulted in an initial accumulation of AuCl2− ions during the first electrodeposition process onto fresh graphite.
Do not hallucinate.

Figure 5. Current and gold concentration with time during electrodeposition on virgin graphite particles in CPBE reactor at +0.20 V (SCE); flow rate= 0.25 dm$^3$ min$^{-1}$

Figure 6 shows images of Au deposits in the CPBE (a) on the feeder Ti cathode and (b) on the graphite particulates in the catholyte compartment. Even Au deposition was observed on the feeder cathode unlike in the packed bed of graphite particulates. On the feeder cathode, the majority of Au deposition occurred along the area corresponding to the draft tube as well as on the feeder cathode area corresponding to the particulates packed bed. Since the voidage in the draft tube and above the packed bed was higher with respect to that in the packed bed, the effective conductivity of electrolyte in those areas was higher, and hence became the preferred paths for the current flow. In order to ensure maximum amount of current passing through the particulates packed bed and to fully utilise the large surface area provided by the graphite particulates to ensure high Au removal rates, the feeder cathode areas corresponding to the draft tube and above the packed bed were insulated (lacquered) with acrylic to block the current routes by-passing the packed bed [10].

![Figure 6. (a)](image-a)(Figure 6. (a))![Figure 6. (b)](image-b)(Figure 6. (b))

**Figure 6.** Images of gold deposits in the CPBE: (a) on the feeder cathode electrode and (b) on the Au particulates inside the catholyte compartment.

The peak in the magnitude of the (negative) reduction current after 3500 s was as a result of the interfacial area increasing with time until the growing nuclei coalesced, while the concentration of dissolved gold in solution decreased. Having metallised the graphite particles, in further electrodeposition experiments at +0.20 V (SCE), >99 % of the gold was recovered from solution in just over 2 hours (figure7). The initial current was nearly double that with the bare graphite, even though the initial concentration current was lower (0.33 mol m$^{-3}$ against 0.44 mol m$^{-3}$), probably
because the kinetics of gold reduction are slower on graphite than on gold. Therefore, while the reduction of \( \text{AuCl}_4^- \) ions to \( \text{Au} \) on a gold surface is mass transport controlled at +0.20 V (SCE), this is not the case on graphite. The conductivity of the particles would also have increased once coated with gold, so more of the bed would have been electrically active.

It can also be seen in Figure 7 that on gold, the reduction of \( \text{AuCl}_4^- \) ions occurs at the same rate as the reduction of \( \text{AuCl}_2^- \) ions. Hence since \( \text{Au}^I \) does not appear in solution, it is possible to follow the electrowinning of gold, at potentials where the reduction is mass transport controlled online via fibre optics by measuring the \( \text{Au}^III \) concentration with UV-Vis spectrometry. However, online measurement is only applicable for a diluted gold concentration (< 1 mol m\(^{-3}\)). The plateau in current of about 4 mA after ca. 8000 s (Figure 7), is probably due to reduction of dissolved oxygen by:

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O
\]  

(5)

The main source of dissolved oxygen was the aqueous \( \text{H}_2\text{SO}_4 \) anolyte, which would have been supersaturated with oxygen and for which Nafion membranes have been reported to have high solubility and diffusion coefficients [11]. For typical Nafion membranes, of 1.78×10\(^{-5}\) m thickness, the diffusion coefficient of oxygen was 5×10\(^{-11}\) m\(^2\) s\(^{-1}\) and the solubility was 15 mol m\(^{-3}\) [12]. As oxygen was generated at the anode of the CPBE reactor, the anolyte dissolved oxygen concentration would have increased and because of the diffusion across the membrane, the catholyte dissolved oxygen concentration would have also increased with time. The maximum current at the 0.1 m\(^2\) area graphite cathode, from the reduction of dissolved oxygen, limited by diffusion across a typical Nafion membrane, was predicted to be 3.3 mA. This reduction of dissolved oxygen decreased the charge efficiency for gold electrowinning to ca. 0.90. However, this loss of efficiency will be less of a problem if the leaching and electrochemical reactors are coupled, since the anolyte will be a chloride solution to generate chlorine which has a much lower solubility and diffusion coefficient through Nafion membranes [12].

![Figure 7](image_url)

Figure 7. Depletion of \( \text{Au}^III \) concentration and current with time during batch recycle electrowinning on gold metallised particles in CPBE reactor with feeder electrode at +0.20V (SCE); flow rate=0.25dm\(^3\) min\(^{-1}\).

The concentration decay during the electrodeposition of gold under mass transport control can be approximated to the general form expected for a model steady-state plug flow reactor (PFR), coupled to a CSTR. Hence, for a mass transport controlled reaction, the concentration should decay exponentially with time according to equation 3.6, and as shown experimentally in figure 8. The \( k_m A_a \) values were measured as 1.1×10\(^{-5}\) m s\(^{-1}\) for deposition on virgin graphite particles and 1.3×10\(^{-5}\) m\(^3\) s\(^{-1}\) for deposition on Au-plated graphite particles:

\[
c_i = c_a \exp \left\{ -\frac{vt}{V} \left[ 1 - \exp \left( -\frac{k_m A_a L}{V} \right) \right] \right\}
\]  

(6)
Figure 8. Depletion of dissolved \( \text{Au}^{III} \) concentration with time during batch recycle reduction in CPBE reactor with feeder at +0.20 V (SCE); 
flow rate = 0.25 dm\(^3\) min\(^{-1}\)

It was considered that increasing the inlet flow rate increased the mass transfer rate within the CPBE and therefore, may increase electrodeposition rates. However, at higher flow rates, the graphite particles were entrained up the draft tube from the bottom of the particle bed faster than they could be replaced by the falling particles from above. Hence, the lower part of the bed was not a descending packed bed in contact with the feeder electrode and was unable to deposit gold at the electrode. Therefore, the overall electrodeposition current at higher flow rates was lower as shown in figure 9.

Figure 9. Effects of flow rate on the time dependency of current, for gold deposition in a CPBE reactor at a feeder cathode potential of +0.20 V (SCE) and an initial gold concentration of 0.5 mol m\(^{-3}\).

It has been shown that gold chloride ions can be depleted from solution by electrodeposition, to concentrations that were analytically undetectable. Gold was recovered with high current efficiencies (figure 10) and very low specific electrical energy consumption (equation 3.7) of 800-1300 kW h (tonne Au)\(^{-1}\) for cell voltages (U) of 2.0-3.0 V and fractional current efficiencies of ca. 0.95.

\[
w / \text{kW h (tonne Au)}^{-1} = \frac{nF}{\Phi_f} \cdot \frac{U}{3.6M_{Au}}
\]  
(7)
3.2 Deposit morphologies

The morphology of the Au deposits was one of the major factors that determine if the CPBE was feasible for the recovery of Au from the catholyte (leach solution). Au deposits formed from a chloride media tend to be dendritic [4],[5], which break from the electrode’s surface easily, re-dissolve in the catholyte and hence, reducing current efficiency. Coherent and adherent Au deposit was essential for maintaining a high current efficiency, achieving a reasonable Au loading on the electrode and enabling the transfer of metals-coated electrode to the electro-refining stage [9].

Figure 11 shows a SEM image of virgin graphite beads which will be used as a cathode in the CPBE. As the density of the graphite particles is recorded ca. 2.5 g cm$^{-3}$, it is essential to metallise the virgin graphite particles. Thus, a layer of gold of at least 5 μm thick was required to increase the effective density enough to prevent the particles floating in a 5 kmol m$^{-3}$ Cl$^{-}$ solution.

Figure 12 depicts a SEM image of Au deposits on a graphite particulate in the CPBE, operating mass transport control, at a feeder cathode potential of +0.20 V (SCE). The average diameter of graphite particulates before and after Au deposition, measured under a microscope, was 520 and 530 μm, respectively which are shown in Figure 12. Therefore, the thickness of the Au deposits was ca. 10 μm.

Subsequently, the metallised graphite particulates were used to deposit Au from the actual WEEE leachate. The morphology obtained at +0.20 V (SCE), Au deposited under total mass transport control were adherent to the particulates and depicts a compact cauliflower structure and little voidage. Random samples of Au particulates had been chosen from the packed bed cathode showed similar structure to that of figure 13, which proved that the constant collisions between the Au particulates in the CPBE were able to improve the morphology of the deposits.
4. Conclusion
Experimental results demonstrated that the CPBE was suitable for the recovery of Au from the leach solution produced by leaching metals from WEEE. Concentrations $<0.5 \text{ mol m}^{-3} (<10^2 \text{ g m}^{-3})$ of AuCl$_4^-$ and AuCl$_2^-$ ions in 4 kmol m$^{-3}$ HCl + 1 kmol m$^{-3}$ NaCl in aqueous electrolyte were successfully reduced to elemental gold in CPBE of 0.5-1 mm graphite particles, in an electrochemical reactor.
incorporating a cation-permeable membrane and operated in bath recycle mode. Depletion to concentrations $< 5 \times 10^{-3}$ mol m$^{-3}$ ($< 1$ g m$^{-3}$) appeared to be mass transport controlled at an applied potential of +0.20 V (SCE) and specific electrical energy consumption (SEEC) of ca. 800-1300 kW h (tonne Au)$^{-1}$ for cell voltages (U) of 2.0-3.0 V and fractional current efficiencies of ca. 0.95. However, atomic absorption and UV spectrophotometry established that, as the ([AuCl$_4^{-}$]+ [AuCl$_2^-$]) concentration decayed, the [AuCl$_2^-$]:[AuCl$_4^{-}$] molar ratio changed. A multi-step mechanism for reduction of AuCl$_4^{-}$ ions proposed by Cheng et al. explained this behavior in terms of changing overpotentials for AuCl$_4^{-}$ and AuCl$_2^-$ reduction as total dissolved gold concentrations decreased. In addition, SEM images confirmed that adherent and coherent Au deposits were achieved with CPBE for Au deposition under mass transport control, which is at +0.20 V (SCE).

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