

# *The use of graphite cloth electrodes for the recovery and separation of gold*

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The electrodeposition and recovery of gold from spent electroplating bath solutions using a graphite cloth electrode in a flow-through cell is described. Optimized conditions of flow rate, current densities, screen potentials and additives were established to achieve high-percentage recoveries and good separation of the Au from admixtures of base metals (Cu, Cd). The results are sufficiently encouraging to serve as the basis for a scaled-up process.

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## 1. Introduction

The steadily increasing price of gold on world markets has made its recovery from any industrial effluent which might contain soluble gold complexes most attractive. This is especially so in the case of electrolytic plating baths, where relatively small volumes of liquid combined with fairly high concentrations of gold are encountered. The solutions used often contain admixtures of base metal ions in addition to the gold; any method for recovering the gold which is at the same time capable of achieving its separation from the latter, will be clearly advantageous. Electroplaters are, by the nature of their calling, familiar with electrochemical techniques and should not find it difficult to apply an electrochemical separation/recovery method to the clean-up of their plant effluent.

Instrumentation suitable for carrying out such an operation, using graphite cloth screen electrodes in a flow-through cell, has been described recently [1]. Since this set-up is adaptable for continuous operation, it was decided to test its performance for the electrodeposition of gold from effluent streams. The work is described here.

## 2. Experimental

The model solution employed contained  $10^{-3}$  M  $\text{AuCl}_3$  and 0.5 M KCl, adjusted to about pH 2 with HCl. In the course of method development,

$\text{CuCl}_2$ ,  $\text{CdCl}_2$  and EDTA were added singly and in mixtures so that the efficiency of the separation of gold from the other two metals could be determined. The construction and pretreatment of the graphite cloth electrodes, the flow cell and instrumental set-up have already been described [1-3]. The metal-coated graphite cloth electrodes were photographed with a scanning electron microscope and the metal-ion concentrations were monitored during the course of the experiments by flame spectroscopy (Perkin Elmer 403 AA). In all experiments requiring the determination of concentrations as a function of deposition time, fractions of the flow were collected for 3 min at a time and tested. The points in the graphs represent averages of these results, computed over 10 min each. Pertinent experimental conditions such as flow rates, potentials, current densities, etc. are reported, where required, in the next section. All potentials are referred to the Ag/AgCl/KCl saturated electrode and throughout this work solutions saturated with air (i.e. without prior removal of dissolved  $\text{O}_2$ ) have been used.

## 3. Results and discussion

### 3.1. Deposition of Au from $\text{AuCl}_3$ solution

The cyclic voltammogram recorded for the  $\text{AuCl}_3 + \text{KCl}$  solution (pH = 2) exhibits a single reduction peak at 0.52 V and a single oxidation peak at 0.94 V (Fig. 1). Peak heights are pH-independent

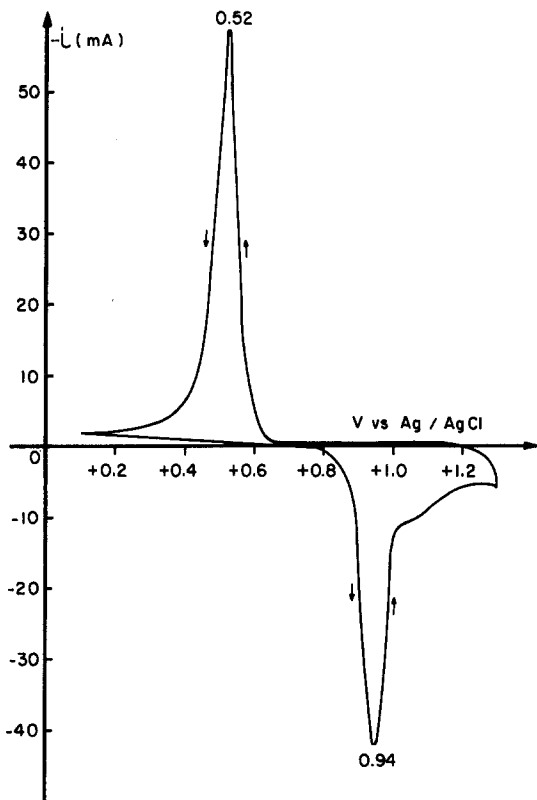


Fig. 1. Cyclic voltammogram of  $10^{-3}$  M  $\text{AuCl}_3$  in 0.5 M KCl (pH = 2) stagnant solution. Rate of potential scan:  $10 \text{ mV s}^{-1}$ .

up to pH 4 and thereafter decrease appreciably [4]. Cycling should not be extended beyond 1.0 V, since the evolution of chlorine has a detrimental effect on the graphite cloth and in addition, chlorine gas bubbles tend to adhere to the screen electrode. Inspection of the voltammogram led to the conclusion that its shape was significantly affected by the reduction of gold ions trapped in the tiny cloth fibres; this leads to departure from pure diffusion behaviour, as observed at solid, nonporous electrodes, and explains the observation that the first peak recorded on a fresh screen was appreciably higher than all the following peaks. Inspection of Fig. 2, which shows a family of reduction curves recorded with the above solution at gradually increasing flow rates, reveals two prominent features. All curves show the 0.52 V gold reduction peak; in those recorded at low flow rates the reduction current then drops to a value nearly independent of the potential applied while at high flow rates it drops slightly and then follows

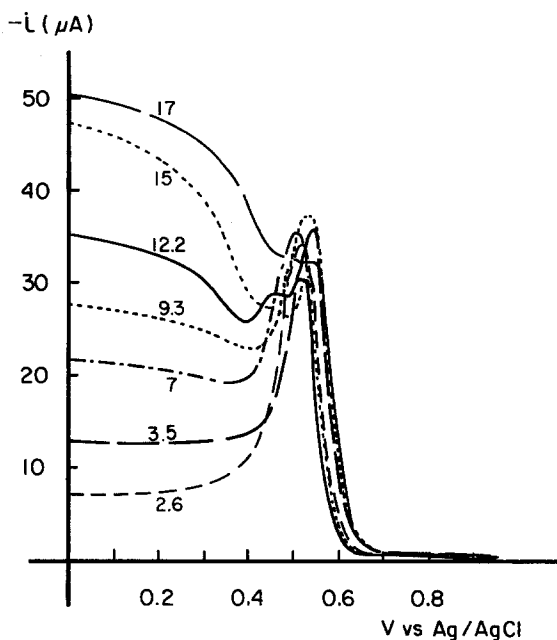


Fig. 2. Reduction current as a function of applied potential, for various flow rates. Solution composition and potential scan rate as in Fig. 1. Flow rates indicated in  $\text{cm}^3 \text{ min}^{-1}$ .

a potential-dependent upward slope. This again fits the presumption of the peak being mainly due to the reduction of Au ions in the solution trapped within the cloth fibres. Information gleaned from these curves served the purpose of this study, i.e. the optimization of both flow rate and applied working electrode potential for a particular case of gold recovery and/or its separation from baser metals. This will be further discussed below.

The general relation between the limiting current  $i_l$  and the flow rate  $v$  has been shown to be [5]:  $i_l = kv^\alpha$ . The value of  $\alpha$  determined experimentally for numerous electrodes (Fig. 3 shows the results obtained with three, chosen at random), was found to be equal to 0.95, a value indicating turbulent flow. The percentage of gold deposited from the model solution flowing through the electrode (held at 0.2 V) was studied for four different flow rates. In each case, deposition is only partial at first (approximately 88% after 30 min), gradually increasing to a value above 98% within 1 h. This may be explained by the continuing narrowing of channels and increase in electrode area (the gold deposits in dendritic crystals, as predicted for high current densities

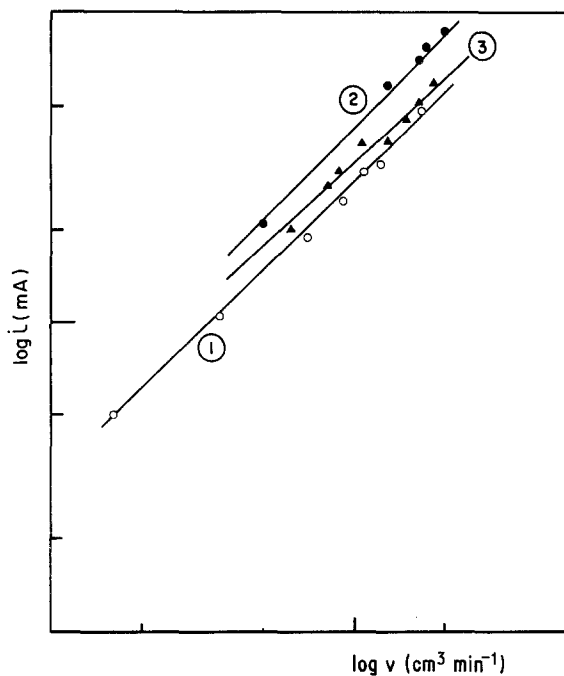


Fig. 3. Log-log plot of limiting current versus flow rate. Solution composition as in Fig. 1. Currents measured at 0.2 V.

[6, 7]). Gold deposition proceeds smoothly up to a coverage of about 1 g Au per cm<sup>2</sup> working electrode area; thereafter, due to the dendritic form of the deposit, parts of it begin to crumble and fall off.

From this point onwards all experiments were carried out at a flow rate of 17 cm<sup>3</sup> min<sup>-1</sup>; the value recommended for the deposition of dendritic Cu [8]. The dependence of recovery percentage on the potential applied to the working electrode was studied at four different values: -0.2, 0.0, 0.2 and 0.4 V, all at the above flow rate. While all percentage recovery versus time curves had the same shape, rising from an initial value to a limiting value near 98%, those recorded at more negative potentials start at higher initial values and attain the limiting value after a shorter time interval. This is, of course, to be expected.

Obviously, whenever Au is to be separated from baser metals, other considerations must be considered. The optimal potential applied is then chosen to obtain minimal contamination of the deposited Au together with maximum percentage recovery.

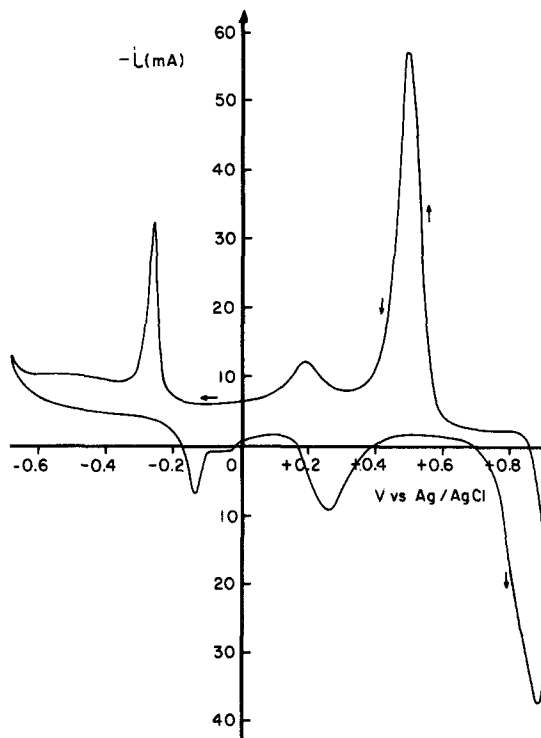


Fig. 4. Cyclic voltammogram of  $10^{-3}$  M  $\text{AuCl}_3$  +  $10^{-3}$  M  $\text{CuCl}_2$  in 0.5 M KCl (pH = 2) stagnant solution. Rate of potential scan: 10 mV s<sup>-1</sup>.

### 3.2. Deposition of Au from an $\text{AuCl}_3/\text{CuCl}_2$ solution

The model solution used in Section 3.1 was modified by the addition of  $\text{CuCl}_2$  up to a concentration of  $10^{-3}$  M. In electrolytic plating baths, whether fresh or spent, the concentration of copper ions is always below that of gold. Fig. 4 shows a cyclic voltammogram recorded in this solution. In addition to the Au peaks already familiar from Fig. 1, two more reduction and oxidation peaks are observed, assignable to the  $\text{Cu(II)/Cu(I)}$  and  $\text{Cu(I)/Cu}$  couples.

On the basis of this voltammogram, electro-deposition at 0.2 V should ensure essentially complete Au recovery, hopefully leaving the copper in solution as a chloride complex. However, in practice, the presence of copper in the solution significantly affects Au recovery. This fact, already observed for cyanide solutions [9] and attributable, in part, to the underpotential of Cu and the overpotential of Au deposition prevailing in their mixtures, is also apparent from an

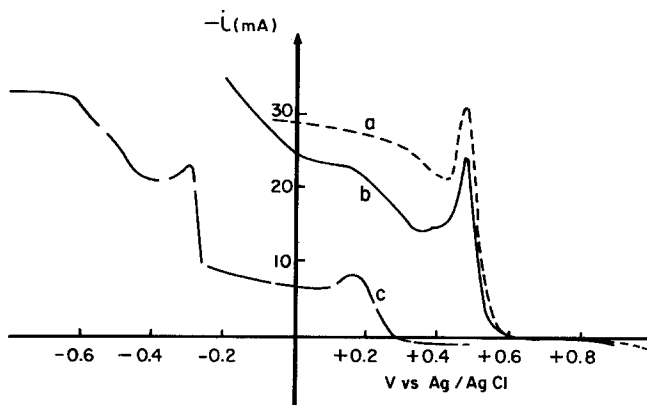


Fig. 5. Reduction current as a function of applied potential, in flowing solution: (a)  $10^{-3}$  M  $\text{AuCl}_3$  in 0.5 M KCl (pH = 2); (b) as (a) +  $10^{-3}$  M  $\text{CuCl}_2$ ; (c)  $10^{-3}$  M  $\text{CuCl}_2$  in 0.5 M KCl (pH = 2). Rate of potential scan:  $10 \text{ mV s}^{-1}$ ; flow rate:  $17 \text{ cm}^3 \text{ min}^{-1}$ .

inspection of Fig. 5. The dependence of Au percentage recovery on applied potential was therefore studied in pure Au and Cu solutions and in a mixture of the two (curves a, b, c, respectively, in Fig. 6).

The results displayed in this figure may be attributed to three factors: (a) the under- and over-potential of Cu and Au mentioned above; (b) the deposition of copper oxides within the potential range encompassing the first copper reduction peak (Fig. 4) (these are soluble in ammoniacal solution and reduce film conductivity and partially block deposition sites); (c) as a direct result of (b), the morphology of the deposited Au changes from dendritic to globular in the presence of copper (Figs. 7a and b), the deposition surface decreases and percentage recovery is lowered to a steady value around 60%. This effect can be observed even with very low copper percentages (about

0.2 at% Cu in the deposited metal film, as determined by atomic absorption after film dissolution). The above considerations point to 0.3 V as the optimal applied potential for adequate recovery of reasonably pure gold from Au/Cu mixtures. The deposited film may be further purified by dissolving the traces of copper oxides present in it with ammonium hydroxide solution.

As a rule, environmental considerations will also require copper ions to be cleared from the solution. This may be done by placing a second screen electrode downstream from the first and applying a potential of  $-0.5 \text{ V}$  to it. This will result in 80% copper recovery during the first 30 min, increasing gradually to above 95% within 1 h. All the Au escaping deposition on the first screen, co-deposits on the second. The potentials recommended in previous studies [1, 8] cannot be applied here, since the presence of Au in the

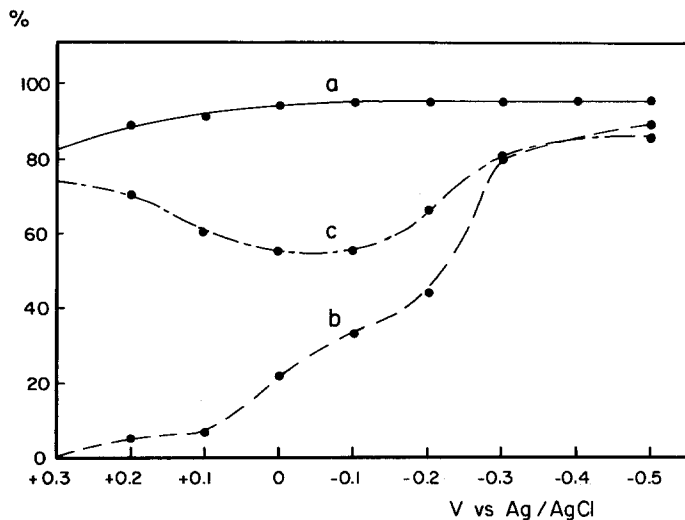


Fig. 6. Metal percentage recovery as a function of applied potential in three flowing solutions, all 0.5 M KCl (pH = 2). (a)  $10^{-3}$  M  $\text{AuCl}_3$ ; (b)  $10^{-3}$  M  $\text{CuCl}_2$ ; (c)  $10^{-3}$  M  $\text{AuCl}_3$  +  $10^{-3}$  M  $\text{CuCl}_2$ .

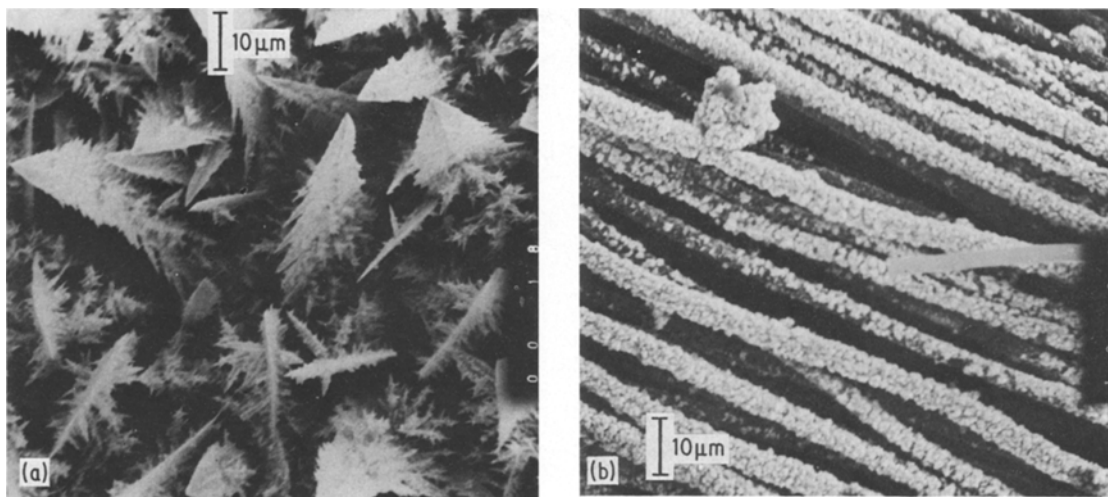


Fig. 7. SEM photographs of metal film deposited (a) from pure  $\text{AuCl}_3$  solution and (b) from an  $\text{AuCl}_3 + \text{CuCl}_2$  mixture. Potential applied in both cases: 0.2 V.

deposited metal film lowers hydrogen evolution overvoltage [10].

### 3.3. Deposition of Au from an $\text{AuCl}_3/\text{CdCl}_2$ solution

The experiments described in Section 3.3 were repeated with an  $\text{AuCl}_3/\text{CdCl}_2$  solution at pH 3.8. In the cyclic voltammogram, the Au peaks were unaffected, while the Cd reduction/oxidation peaks appeared at  $-0.95$  and  $-0.36$  V respectively. This indicates that the separate electrodeposition of Au and Cd from their mixture presents no problem whatever. Satisfactory results in flowing solution were obtained: 99.95% pure gold was deposited on the first screen held at 0.0 V, while Cd was deposited at a percentage recovery exceeding 90% on the next screen, held at  $-1.0$  V. At pH 3.8, hydrogen evolution at  $-1.0$  V was negligible.

### 3.4. Enhanced $\text{AuCl}_3/\text{CuCl}_2$ separation by Cu-EDTA chelation

The addition of EDTA, a component frequently found in electroplating baths at the appropriate concentration and pH, will transform the Cu present into its soluble Cu-EDTA complex and concomitantly significantly increase the separation between the Au and Cu reduction peaks. To the model solution used in Section 3.2,  $2 \text{ g dm}^{-3}$

EDTA were added and its pH adjusted to 3.8. The choice of pH is dictated by the limits set on the one hand by EDTA solubility (which becomes increasingly insoluble in acid solution) and, on the other, by the minimum pH required for copper ion chelation. A cyclic voltammogram recorded in a stagnant solution of the above composition shows the potential of the Au peak to be unaffected by the EDTA addition (although it is somewhat broader and lower); only a single Cu reduction peak is observed, at  $-0.65$  V.

Au is deposited from this solution on the first screen, held at 0.2–0.0 V, at efficiencies equal to those cited in Section 3.1; it is, in addition, essentially free of co-deposited copper (as compared to the results reported in Section 3.2). The Au deposit retains its dendritic form. The deposition of Cu on the second screen, held at  $-1.1$  V (the most negative potential applicable before causing  $\text{H}_2$  evolution), is incomplete under these conditions with recovery percentages ranging around 50%. The same approach is applicable to the deposition and practically complete recovery of pure Au from Au/Cd/Cu mixtures in KCl-EDTA solution.

## 4. Final recovery of the electrodeposited Au

Electro-oxidation of the gold deposited on the screen electrodes fails due to at least two causes: (a) the dendritic crystals are apt to become

detached before complete dissolution and collect in the form of a gold slurry in the cell; and (b) thin gold films require positive overvoltages at which  $\text{Cl}_2$  is released from the KCl solution, attacking the electrode and blocking its area. In view of this, chemical dissolution in a small volume of hot, concentrated HCl containing 10% concentrated  $\text{HNO}_3$  was found vastly preferable. The coated screens are taken out of the cell, placed over a container and the dissolving acid mixture poured through them. On a bigger screen, mechanical separation of a major part of the gold (by scraping, etc.) should be possible. The remaining graphite-gold mixture may easily be pulverized and separated by established separation methods.

Both the acids used in the chemical dissolution process and the mechanical removal process gradually cause the deterioration of the screen electrodes. The enormous price difference between the graphite cloth and that of the recovered gold, whether in the form of an ionic solution which can immediately be used to replenish electrolytic baths or as metallic gold for other uses, makes their sacrificial use economically acceptable.

Summing up the results described in this study,

the authors venture to submit that they may serve as the basis for a scaled-up version for the efficient and economical recovery and/or separation of Au from streaming solutions containing base metal admixtures.

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