A study of the influence of copper on the gold electrowinning process

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Synopsis

Electrowinning is an attractive method to recover gold from the relatively concentrated aurodicyanide solutions produced by the elution of loaded carbon, provided that the plated gold can be easily removed using high pressure water sprays. In practice, difficulty with the removal of the gold is occasionally experienced and has been correlated with the presence of high concentrations of copper in the eluate. In this work, the influence of copper on the electro-plating of gold was further investigated using a laboratory electrowinning cell with a rotating disc cathode, polarization, and adhesion tests. It was found that the reduction of copper will compete with gold electrowinning at high copper tenors and that the adhesion of the precipitated gold is also increased under these conditions.

Keywords: reduction, adhesion, morphology, current efficiency, limiting current.
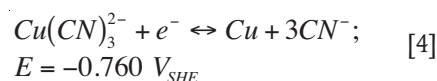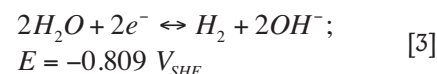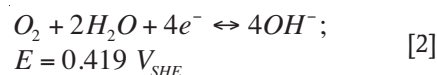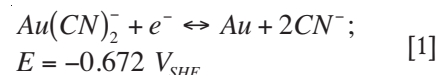
Introduction

Electrowinning is best suited to the partial recovery of gold from solutions with high gold tenors. Furthermore, no foreign ions are introduced into the solution and it can also be efficiently operated at higher temperatures. High grade gold can be produced that requires no further purification, provided that the solution to be treated does not contain metal ions that will be plated during electrowinning. Unfortunately, this is an idealized assumption because base metals such as silver, copper, nickel, cobalt and iron typically occur with gold in the electrolyte as cyanide complex ions and may be plated out during electrowinning. A major disadvantage of the gold electrowinning process is its inability to produce discardable tailings. This is mainly due to the cathodic shift in the reduction potential of the $Au(CN)_2^-/Au$ half reaction when the gold in solution decreases, resulting in preferential deposition of base metals, and also a decrease in the mass transfer rate of aurodicyanide to the cathode surface, which may cause a significant decrease in the efficiency of the electrowinning process.

Base metals may influence the gold electrowinning process when present in high concentrations relative to that of gold or when too high overpotentials are applied. Base metals can adversely affect the electrowinning process in terms of decreased current efficiencies, poor bullion fineness, passivation of the cathode surface[1] and by influencing the morphology of the plated gold.

Theoretical background

Thermodynamics of gold electrowinning

The following electrochemical reactions are of relevance during the gold electrowinning process (E values quoted for metal ion concentrations of 10^{-4} mol.dm^{-3}, NaCN concentration of 0.2% and NaOH concentrations of 2%):

$$Au(CN)_2^- + e^- \leftrightarrow Au + 2CN^-;$$
$$E = -0.672 \ V_{SHE} \quad [1]$$

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-;$$
$$E = 0.419 \ V_{SHE} \quad [2]$$

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-;$$
$$E = -0.809 \ V_{SHE} \quad [3]$$

$$Cu(CN)_3^{2-} + e^- \leftrightarrow Cu + 3CN^-;$$
$$E = -0.760 \ V_{SHE} \quad [4]$$

The gold, which is present in the solution in the form of aurodicyanide ($Au(CN)_2^-$), is reduced to metallic gold, according to Reaction [1] at potentials more negative than the reversible potential. Reaction [2], representing oxygen reduction in alkaline solutions, is another cathodic reaction competing with gold deposition. This is mainly because the

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electrolyte is likely to be saturated with oxygen due to the oxygen evolution occurring at the anode. Reaction [3] represents the evolution of hydrogen, which occurs at a significant rate at potentials more negative than -0.96 V_{SHE} when working at pH values above 10.[1] The evolution of hydrogen should be under kinetic control at a significant range of potentials more negative than -0.96 V_{SHE} and therefore consumes a high proportion of the cathodic current. The major anodic reaction is the oxidation of water to oxygen, also indicated by Reaction [2].

The reduction reaction of cuprous cyanide ($Cu(CN)_3^{2-}$) to metallic copper is indicated in Reaction [4]. The more negative potential for the reduction of cuprous cyanide to metallic copper than that for the reduction of aurodicyanide to metallic gold, signifies that gold should plate preferentially to copper at these conditions. However, copper may co-deposit with gold if high overpotentials are applied, or when the copper concentration is high relative to that of gold.[2]

Polarization diagrams

The kinetics of electrochemical reactions are typically studied by conducting polarization experiments in which the current required to change the potential of the electrode may be determined. If the potential of the electrode is changed at a continuous rate, so-called potentiodynamic polarization diagrams are obtained.

While it is relatively easy to obtain polarization data, the interpretation is often difficult, as more than one reaction may contribute to the currents measured. Thus, it is preferable to first simplify the investigation of industrial systems by characterizing a purer electrolyte and then sequentially adding species that may contribute to further electrochemical reactions. In this way the contributions of the individual reactions may be isolated, if it can be assumed that interaction between the species will be minimal.

Morphology and adhesion of the plated gold

From an industrial point of view, it is essential to obtain loosely adherent precipitates that can be easily removed with high pressure water. If this cannot be achieved, some gold will get locked up inside the electrowinning cells, which can result in electrowinning being uneconomical. The electrolyte temperature, current density, and conductivity of the electrolyte have typically proved to be the main variables that influence the adhesion of gold precipitates.[3] Co-deposition of base metals, such as copper, may also have an effect on the morphology and adhesion of the precipitate.

Experimental

The electrodeposition of gold in industrial electrowinning cells is typically operated under mass transfer control. To realistically simulate this and to obtain repeatable results, it is necessary to control the rate of mass transfer to the electrode. This can be conveniently done using a rotating disc electrode for which mass transfer correlations are well known. The rate of mass transport to the electrode surface is a function of the angular velocity of the rotating disc as indicated by the Levich equation below:

$$i_L = 0.62nFv^{-1/6}D^{2/3}C\omega^{1/2} \tag{5}$$

where, i_L = limiting diffusion current density (A/cm2)
n = number of electrons transferred
F = Faraday's constant (96 485 C/mol electrons)
v = kinematic viscosity (m2/s)
D = diffusion coefficient (m2/s)
C = concentration (mol/ dm3)
ω = angular velocity (rad/s).

From Equation [5] it is evident that a direct relation exists between the limiting current and the square root of the angular velocity. The angular velocity was varied and the subsequent limiting current measured, in order to determine if the reaction is mass transfer controlled. On basis of this, an angular velocity of 1200 rpm. was selected for all test work.

For the rotating disc tests, a 500 ml Perspex beaker, in which the rotating disc was placed together with two carbon counter electrodes symmetrically on either side of the rotating disc, was used as cell. The working electrode, counter electrodes and reference electrode were connected to an ACM Gill AC potentiostat.

The cathode was an 8 mm diameter, 304 stainless steel rod with length of 7.5 mm, mounted in a non-conductive plastic cylinder, leaving an exposed area of 0.5 cm2. The cathode was polished, to a mirror finish, with 0.25 micron diamond paste. Electrical connection to the electrode was achieved through a threaded rod screwed into the back of the cylinder. Contact between the sides of the electrode and the electrolyte was prevented by fitting it into a Teflon sleeve with a diameter of 15 mm. As reference electrode, a silver/silver chloride electrode with a Luggin tube was used, the end of the Luggin tube placed just beneath the rotating disc. The Luggin tube salt bridge was filled with a saturated potassium chloride solution. Impedance tests were done before each test to determine the resistance of the electrolyte between the cathode and the tip of the Luggin probe, and the potentials were adjusted using Ohm's law.

Synthetic solutions were prepared by AngloGold's West Wits assay laboratories to simulate plant conditions. The electrolyte was prepared by adding 2 per cent caustic soda together with 0.1 per cent CN, which simulates conditions normally encountered in practice. Chemical compositions typically ranged from low to high copper and gold concentrations in order to determine at which concentrations the influence of copper became problematic. The solution temperature was kept constant at 25°C for all test work by immersing the Perspex beaker in a water bath. The influence of gold and copper at various concentrations was studied by conducting potentiodynamic tests using an ACM Gill AC potentiostat. Potentiodynamic scans were done from 0 to -2.5 V at a scan rate of 3 mV/s. The applied potential and the resulting current were stored on a personal computer using data acquisition software.

The adhesion of the precipitates was determined by a pull-off test using Scotch tape. The degree of adhesion was rated on a scale of 1 to 5, with 1 being very loosely adherent and removable with slow flowing water, 2 fully removable with Scotch tape, 3 partially removable with Scotch tape (more than 50 per cent removed), 4 partially removable with Scotch tape (less than 50 per cent removed), and 5 highly adherent and only removable with 600 grid sanding paper.

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The morphology of the deposited metal was studied using a scanning electron microscope.

Results and discussion

Polarization diagrams

The influence of the gold tenor on the polarization behaviour of the stainless steel electrode is shown in Figure 1.

A positive shift in the potential, where the gold reduction could be noticed, from -1.09 V_{SSE} to -0.95 V_{SSE} at a current density of 0.85 mA/cm^2 can be observed when the gold in solution concentration is changed from 5 ppm to 1 000 ppm. This signifies that, during the electrowinning process, the potential for gold reduction will also shift to more negative potentials as the gold is removed from the solution. This may result in a change in the rate-limiting step of the electro-chemical reaction from diffusion control to chemical control when a constant potential is applied. A decrease in the current density at an applied potential of -1.0 V_{SSE} can also be observed when the gold in solution concentration decreases, as indicated in Figure 1.

As mentioned, copper may co-deposit with gold when present in high concentrations relative to the concentration of gold. From Figure 2 it is evident that copper, present in concentrations of 200 ppm and higher, will plate preferentially to gold present at 5 ppm. At these concentrations the current density for the copper reduction reaction is higher than that for the gold reduction reaction at an applied potential of -1.0 V_{SSE}. Copper will therefore plate at a faster rate than gold under these conditions.

Although the current efficiency for gold electrowinning is expected to decrease as copper co-deposits with gold, the rate of gold electrowinning should remain the same, whether copper is present in the solution or not. This is because, at a specific applied potential, the limiting current for gold reduction should be independent of the copper concentration, assuming that the electrode potential will be such that the rate-determining step for gold deposition will be the mass transfer of aurodicyanide to the reaction interface.

Influence of the metal ion concentration on the adhesion of the precipitate

Very loosely adherent precipitates were obtained when gold was plated from solutions containing only gold. These precipitates were easily removable with Scotch tape. On the other hand, copper plated from pure copper containing solutions proved to be moderate to highly adherent. Table I gives an indication of the degree of adhesion of the precipitates.

As indicated in Table I, some of the precipitates came off in two layers, with the bottom layer being more adherent than the top layer. A good example of this is the 2 000 ppm Cu precipitate where the top layer came off extremely easily (removable with flowing tap water) while a highly adherent bottom layer remained, which had to be removed with 600 grid sanding paper. The morphologies of these layers are shown in Figure 3:

From Figure 3 it is evident that the top layer plated in a more dendritical fashion, while the bottom layer deposited with a basal structure. The highly adherent bottom layer deposited as very small grains, packed tightly together. In contrast to this, much larger grains were observed for the loosely adherent top layer. The two different morphologies are possibly due to a change in the fluid dynamics during the electrowinning cycle. The hypothesis for this phenomenon is that at the beginning of the cycle, mass transfer to the cathode might have been slow. This allowed ample time for the copper atoms to reach the lowest energy locations on the cathode, resulting in a fine grained, basal and very adherent precipitate. As copper started to precipitate, the cathode surface became rougher, thereby causing an increase in agitation and subsequently an increase in the rate of mass transfer, resulting in a more dendritic morphology for the top layer of the precipitate.

Table I also indicates that gold that was deposited from solutions containing high gold concentrations, typically 1 000 ppm Au and 500 ppm Au, proved to very loosely adherent while the precipitates obtained from low gold concentrations, typically 100 ppm Au and 5 ppm Au,
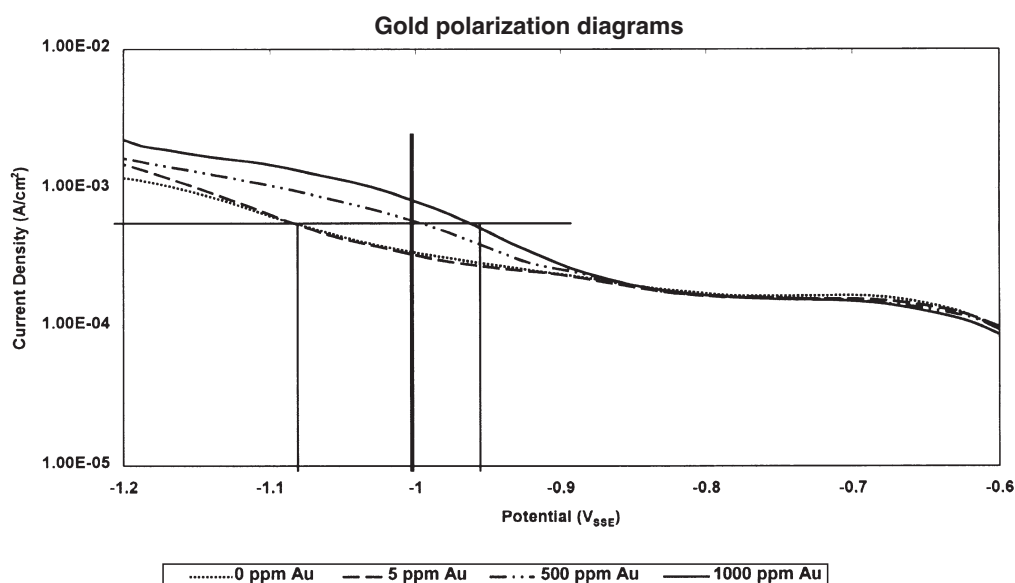

Figure 1—Potentiodynamic results for various gold concentrations (1200 rpm; 25°C; 2% NaOH; 0.1% CN)

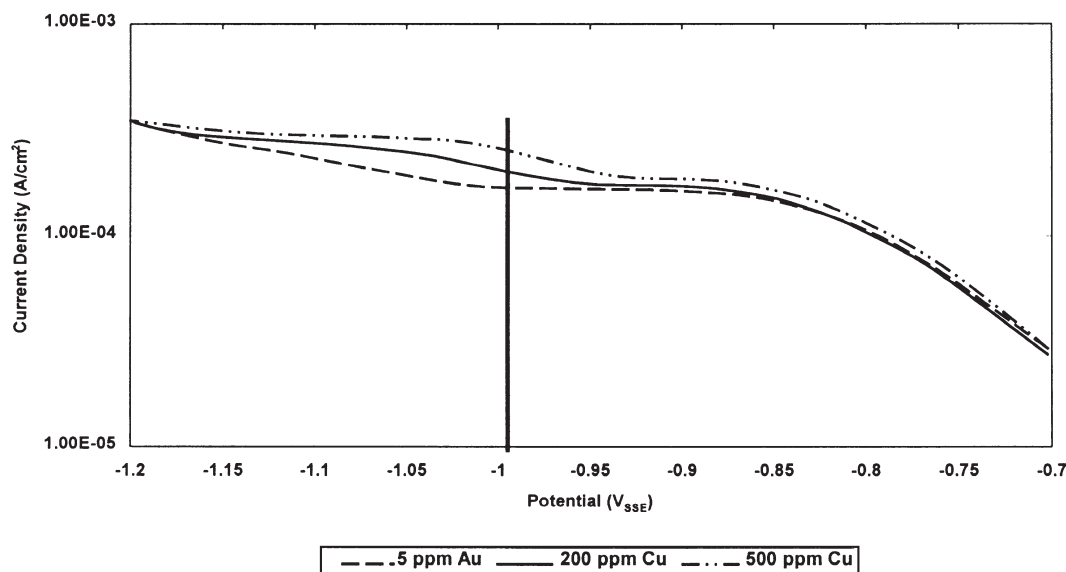# A study of the influence of copper on the gold electrowinning process

Figure 2—Polarization diagrams illustrating the effect of high and low copper concentrations (1200 rpm; 25°C; 2% NaOH; 0.1% CN)

Table I

Indication of the adhesion of the obtained precipitates (-1.0 V$_{SSE}$, 2% NaOH, 0.1% CN, 25°C, 1 200 rpm, 14-hour cycles)

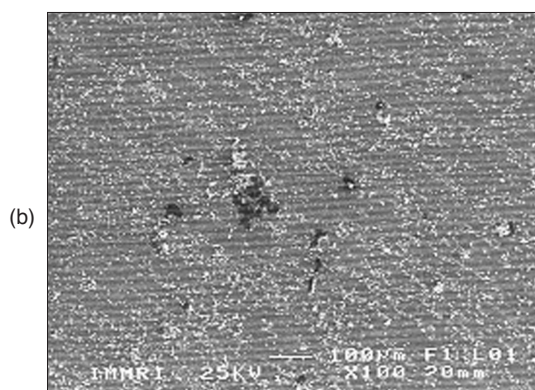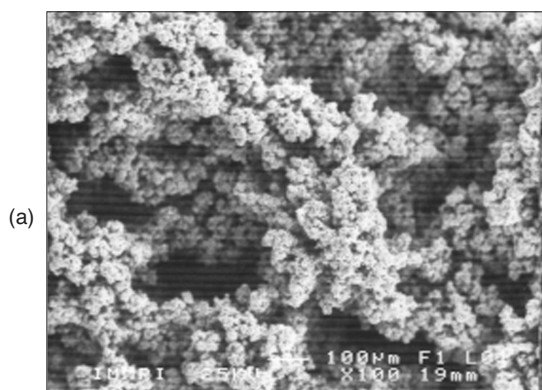| Adhesion	1 000 ppm Au	500 ppm Au	100 ppm Au	5 ppm Au	2 000 ppm Cu	1 000 ppm Cu	500 ppm Cu
Top layer	1	1	2	3	1	2	4
Bottom layer	N/A	2	N/A	N/A	5	3	N/A

Figure 3—SEM images of the precipitate produced from the solution containing 2000 ppm copper, (a) top layer (b) bottom layer. (-1.0 V$_{SSE}$, 2% NaOH, 0.1% CN, 1 200 rpm, 25°C)

deposited moderately adherent. The morphology of the deposited gold from solutions containing 1000 ppm Au and 5 ppm Au is shown in Figure 4.

From Figure 4 it is clear that the gold that precipitated from the 1 000 ppm Au solution deposited as much larger grains than the gold that was precipitated from solution containing 5 ppm Au. It is therefore apparent that precipitates with a fine grained structure will be highly adherent, while more loosely adherent precipitates are expected for coarse grained precipitates.

Observations made in industrial electrowinning cells indicated that a thin adherent metallic layer remained after washing the cathodes with high pressure water. Taking the above-mentioned scenarios for gold and copper into account, the following explanation can be given for this occurrence: When copper is present in very high concentration in the electrolyte, typically 2 000 ppm, while gold is present in concentrations of less than 500 ppm, the reduction potential for cuprous cyanide to metallic copper is more positive than that for the reduction of aurodicyanide to metallic gold. Consequently, copper will co-deposit with gold at a significant rate. During this period a precipitate similar to that indicated in Figure 3(b) may be obtained, resulting in a highly adherent initial precipitate. As the copper concen-
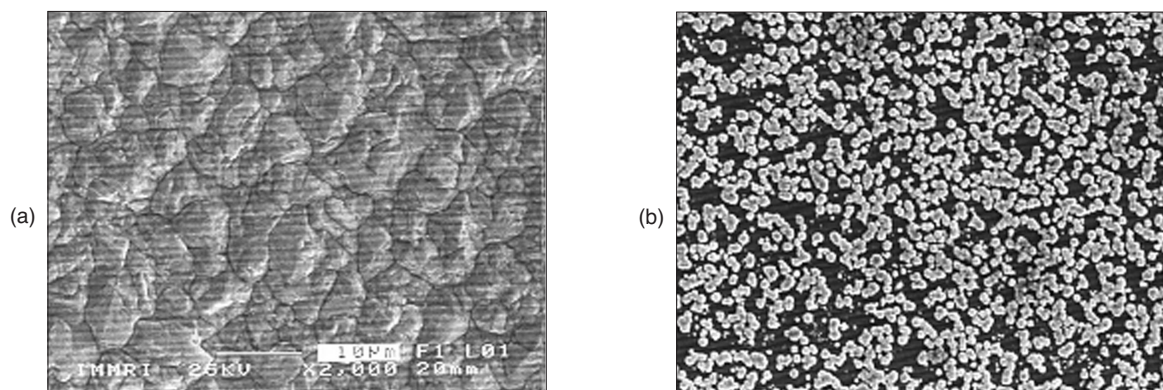
Figure 4—SEM images of the precipitated gold from (a) 1 000 ppm Au solution, and (b) 5 ppm Au solution (-1.0 V_{SSE}, 2% NaOH, 0.1% CN, 1200 rpm, 25°C)
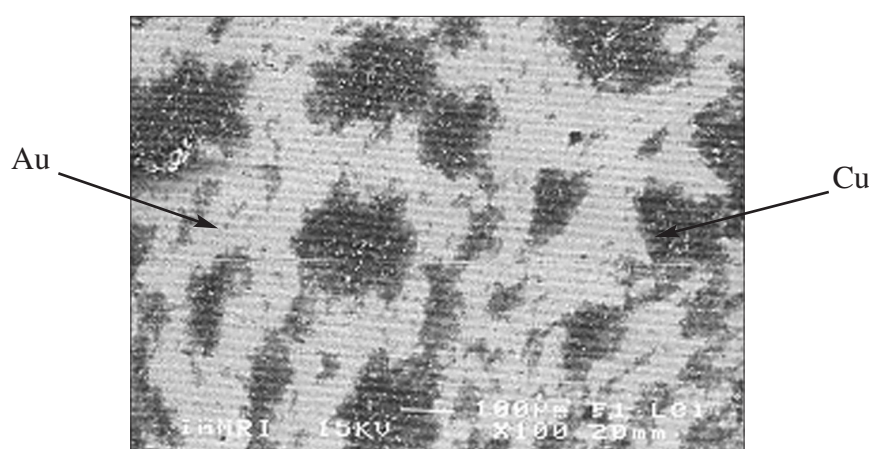

Figure 5—SEM image obtained from a solution containing 100 ppm Au and 1 000 ppm Cu. (-1.0 V_{SSE}, 2% NaOH, 0.1% CN, 1200 rpm, 25°C, 6 hours)

tration in solution decreases, the current efficiency for gold electrowinning will increase. The adherent metallic layer that remains on the cathode surface after washing may therefore be because of a small grained, tightly packed copper. It is possible that the co-deposited gold may be encapsulated by this highly adherent copper layer, which will result in gold lock-up inside the electrowinning cells. This effect was characterized by adding 1 000 ppm Cu to a solution initially containing only 100 ppm Au. This resulted in a change in the adhesion of the precipitated metal from a level 2 to a level 4. A 'patch-like' precipitate was obtained where most of the gold and copper plated separately in certain areas of the cathode. An SEM image of this precipitate is shown in Figure 5, where the lighter areas indicate the precipitated gold and the darker areas the precipitated copper.

Influence of applied potential on the morphology of the precipitate

Different morphologies are expected when gold is deposited at different applied potentials. Figure 6 illustrates the difference in the morphology when gold was deposited from a solution containing 1 000 ppm Au at an applied potential of -1.0 V_{SSE} (Figure 6a) and -1.4 V_{SSE} (Figure 6b). It is evident that a more dendritical precipitate is obtained when a potential of -1.4 V_{SSE} is applied.

The reason for the different morphologies is most likely because of the difference in the mass transfer rate for the two

applied potentials where hydrogen evolution was much more copious at -1.4 V_{SSE} than at -1.0 V_{SSE}. Gold that plated at an applied potential of -1.0 V_{SSE} had ample time to diffuse to more favourable sites on the cathode than gold that plated at -1.4 V_{SSE}. The dendritical precipitate obtained at an applied potential of -1.4 V_{SSE} was easily removable with slow flowing water (level 1 adhesion) while the fine grained precipitate obtained at -1.0 V_{SSE} proved to be only removable with Scotch tape (level 2 adhesion). It can therefore be expected that a more loosely adherent precipitate can be obtained when a large overpotential is applied.

Although large overpotentials yield loosely adherent precipitates and optimum potential, in terms of the rate of gold electrowinning and the adhesion of the precipitate, should be determined. Figure 7 shows the rate of gold electrowinning as a function of applied potential.

From Figure 7 it is evident that a decrease in the rate of gold electrowinning occurs when too high overpotentials are applied. This is likely to be due to a decrease in the effective cathode area available for electrowinning because of the enhanced hydrogen evolution, as well as dislodging of the gold from the cathode surface due to the increased surface turbulence caused by the evolution of hydrogen gas.

For this study, the optimum applied potential proved to be -1.2 V_{SSE}, since the fastest electrowinning rate was obtained at this potential and a more loosely adherent

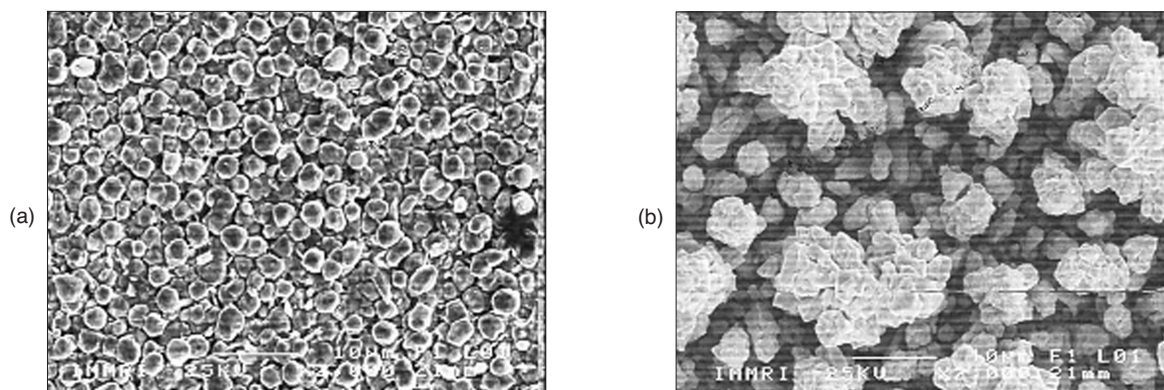# A study of the influence of copper on the gold electrowinning process

Figure 6—Morphology of the precipitated gold at an applied potential of (a) -1.0 VSSE and (b) -1.4 V_{SSE} (1 000 ppm Au, 2% NaOH, 0.1% CN, 25°C, 1 200 rpm)
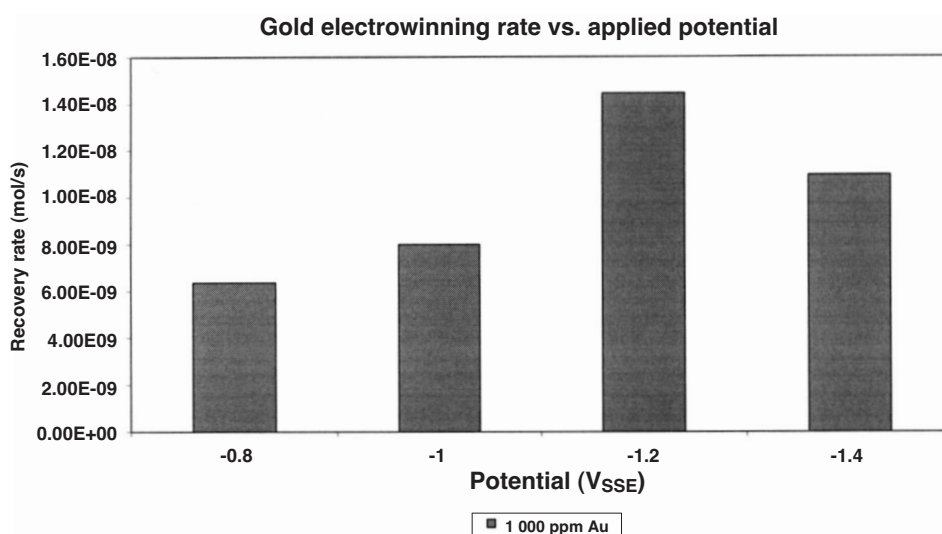

Figure 7—Influence of the applied potential on gold electrowinning rate (1 000 ppm Au, 2% NaOH, 0.1% CN, 25°C, 1 200 rpm)

precipitate can be expected than for gold plated at an applied potential of -1.0 V_{SSE}.

Conclusions

Although copper will co-deposit with gold during the electrowinning process, relatively high grade gold can still be produced by controlling the potential of the cathode. While the presence of copper will lead to a decrease in the current efficiency for gold recovery, the rate at which gold is recovered should remain unaffected if a constant potential is applied.

Observations made during this study indicated that the influence of copper on the adhesion of the obtained precipitate is of greater importance than its influence on the electrowinning performance in terms of the rate and current efficiency. Highly adherent precipitates were obtained when copper and gold were plated from solutions containing high copper concentrations, typically at concentrations higher than 500 ppm Cu. The level of adhesion of a gold precipitate obtained from a solution containing 100 ppm Au increased significantly when 1 000 ppm Cu was added to the solution. Large grained precipitates were obtained when gold was plated from solutions containing high gold concentrations. These precipitates were very loosely adherent. Lower gold

concentrations yielded fine grained, moderately adherent precipitates.

More loosely adherent precipitates are expected when gold is plated at higher overpotentials. Although the adhesion decreased with an increase in the overpotential, a decrease in the rate of gold recovery occurs when too high overpotentials are applied; this is probably due to the removal of loosely adherent gold by the copious evolution of hydrogen gas on the surface of the electrode. In general, potentials more negative than that needed to operate under mass transfer control would only serve to promote other reduction reactions, which is typically undesirable.

Acknowledgements

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