A Study of Certain Problems Associated with the Electrolytic Refining of Gold

Eugen Schalch and Michael J. Nicol

National Institute for Metallurgy, Randburg, South Africa

Metal of high purity is required for many industrial applications of gold. Electrolytic refining is therefore increasingly used in the production of gold from mine bullion and from scrap. The factors affecting the efficiency of the process and the quality of the product are reviewed in the light of studies carried out in association with the Rand Refinery Ltd.

The electrolytic refining of gold forms part of the operations carried out at the Rand Refinery Ltd., Germiston, South Africa. This establishment, described in detail by Adamson (1), refines gold bullion received from the South African gold mines. This mine bullion typically contains up to 12 per cent silver, 2 or 3 per cent base metals and traces of platinum-group metals. The standard refining technique applied to the raw gold is the Miller process (2) which consists of the passing of chlorine through the molten metal. The base metals and the silver are converted to their respective chlorides which are either volatile or report in the slag. Gold that assays about 99.6 per cent is obtained and is poured into gold bars or cast into anodes.

The Miller process can be used to produce gold of 99.99 per cent purity. However, this results in considerable volatilisation of the gold in the form of its chloride for the recovery of which elaborate methods are required. Moreover, gold that is to be used for coins or jewellery must be free from osmiridium which does not alloy with the gold and is not removed in the Miller process.

For these reasons, part of the gold pre-refined by chlorination is subjected to electrolytic refining. This process, carried out in hot acidified chloride solutions, was patented in 1908 by Wohlwill (3) and is thus the oldest industrial application of chloride hydrometallurgy, which has recently become a focal point of increasing attention (4).

The anodes, containing about 0.4 per cent silver and platinum-group metals, are readily dissolved by the passing current in the chloride electrolyte. The gold which is dissolved from the anodes is deposited on the cathodes. The silver liberated from the anodes is precipitated as silver chloride, and cathodic deposition of it and other impurities from the anodes does not occur. After washing of the cathodes with thiosulphate solution to dissolve the silver chloride

that is occluded in the deposit, gold of 99.99 per cent purity or better can be obtained. This corresponds to an impurity level of 100 ppm or less, most of which is silver chloride.

There are problems associated with this process which have their origin in either one or two of the three components of the electrolytic cell: the anode, the electrolyte, and the cathode.

The anodic dissolution of gold in chloride solution produces predominantly gold(III) although a small amount of gold(I) is also formed which is unstable in the electrolyte and undergoes the disproportionation reaction:

This reaction gives rise to the formation of gold fines which report in the cell sludge and must be recycled. As the amount of such gold fines can be as high as 10 to 15 per cent of the throughput, a major objective must be to reduce the extent of reaction (1).

The presence of gold(I) and gold fines can, as will be described later, also have a detrimental effect on the cathodic gold deposit. This deposit is generally very rough and often dendritic, and can lead to bridging between anode and cathode, resulting in electrical shorting of the cells and consequent loss of production. Furthermore, at the Rand Refinery, the purity of the cathodically deposited gold was often found to be below 99.99 per cent and thus did not reach the required standard of purity.

With a view to overcoming these problems, an investigation was carried out in two stages. The first of these involved laboratory-scale experiments aimed at a fundamental understanding of the various reactions involved. The second comprised pilot-scale experiments which were carried out with the aim of applying to operations at the plant the knowledge that had been gained during the first stage.

Fig. 1 Variation of x with the rotational speed of the disc electrode at two different current densities

Fig. 2 Variation of x with the current density at various temperatures

Anodic Dissolution of Gold

As any gold(I) present in the electrolyte originates at the anode, it seemed of primary importance to identify the conditions required to minimise the amount of gold(I) formed during the anodic dissolution process. For this purpose, a given amount of gold was deposited electrolytically on a rotating platinum-disc electrode. This gold deposit was subsequently dissolved anodically under carefully controlled conditions (current density, stirring rate, temperature, chloride concentration) and the charge required for the complete dissolution of the deposited gold was measured. As the formation of gold(I) is an intermediate step in the anodic dissolution of gold, the reactions that occur can be formulated as follows:

where s represents the surface species, and b represents the bulk species. All the gold is oxidised to gold(I) in reaction (2) above. A fraction x of this gold(I) is oxidised further to gold(III) at the electrode surface by reaction (3) whereas the rest of the gold(I), the fraction $1-x$, escapes into the bulk of the solution as gold(I). It is intuitively clear that under otherwise equal conditions an increase in the stirring rate

should cause more gold(I) to be swept away from the anode surface before it can be oxidised to gold(III) and that this should lead to a decrease of x . The effect of the other variables of interest is less obvious.

The determination of the quantity x was based on the charge required to dissolve a known amount of gold, in terms of which, passage of one faraday will dissolve one mole of gold as gold(I) but only one third of a mole as gold(III). Considerations of this kind lead to a quantitative expression of x as a function of dissolution current and time.

Some results of these experiments are given in Figures 1 and 2 (for a more extensive treatment see (5)). Figure 1 shows that x decreases with increased stirring as expected, whereas it increases with the anodic current density. From Figure 2 it can be seen that x increases with decreasing temperature. A further result of these measurements was that x increased with decreased concentration of chloride. Thus it can be concluded that the following operating conditions will help to reduce the production of gold(I) at the anode:

- (1) Low stirring intensity
- (2) High anodic current density
- (3) Low temperature
- (4) Low chloride concentration

A quantitative description of these various effects in terms of reactions (2) to (4) has been derived and will be published elsewhere.

Disproportionation of Gold(I)

Metastable solutions of gold(I) can be prepared by the careful reduction of gold(III) with a suitable reducing agent such as iron(II). The rate of disproportionation of the gold(I) prepared in this way was determined by an electrochemical method.

The results obtained show that the rate increases rapidly with the gold(I) concentration. This strong dependence of the rate on the concentration of gold(I) presumably accounts for the fact that most of the fines tend to accumulate under the anodes in the cells, that is, in that region where the concentration of gold(I) is the highest. It should also be emphasized that the rate of disproportionation is extremely slow (half-lives of the order of hours) and the accumulation of gold(I) in the cells, at concentrations exceeding those thermodynamically possible, is probable.

Cathodic Deposition of Gold

As indicated above, gold cathodes produced on the plant are generally highly dendritic and voluminous. Apart from the obvious difficulties of handling such cathodes and the problems with frequent shorting of the cells, it was felt that an improvement of the deposit morphology could also result in higher cathode purity because of the increased ease of the washing out from the deposit of the occluded silver chloride, the major impurity. Emphasis was therefore laid on the identification of the factors that give rise to dendritic cathodes and of the methods that would improve the morphology of the deposit.

The effects on the deposit morphology of variables such as current density, temperature, agitation and composition of the electrolyte were studied by use of both rotating-disc (to control the agitation) and stationary-plate electrodes. These experiments showed that equilibrium amounts of gold(I) in the solutions gave rise to deposits that were markedly rougher than those obtained from electrolytes that were free of gold(I).

A possible reason for this detrimental effect of gold(I) can be deduced from Figure 3 which shows current *versus* potential curves obtained with gold chloride solutions by changing continuously the potential applied to a gold plated platinum-disc electrode and at the same time recording the current flowing through the electrode. The cathodic current due to the reduction of dissolved gold to gold metal is shown as a negative current in Figure 3. A change to more cathodic potentials is seen to yield higher cathodic currents

due to the increased rate of gold deposition and is thus tantamount to an increase in the driving force of this reaction. The role played by the potential in an electrochemical reaction is therefore very similar to that played by the temperature in a non-electrochemical reaction. As the absolute value of the potential cannot be measured, a saturated calomel electrode (SCE) was employed in this work as a reference. The potential of this electrode measured against the normal hydrogen electrode is + 0.250 V.

The curve shown in Figure 3 for the solution containing 0.05 M gold(III) at 20°C, shows a clear limiting-current plateau corresponding to the diffusion-controlled deposition of gold from gold(III). An increase of the temperature to 50°C brings about an increase in the limiting current — though the plateau for this is not shown in Figure 3. If part of the gold(III) contained in the solution is reduced to gold(I) the voltammogram changes markedly: another limiting-current plateau appears at more positive potentials. This plateau is due to the diffusion-controlled deposition of gold from bulk gold(I). Since in practice only a few per cent of the gold content of the electrolyte is present as gold(I), the deposition from gold(I) occurs under diffusion control at the cathodic potentials required to obtain a reasonably high rate of deposition from gold(III).

However, as is well known (6) from investigations of the cathodic deposition of many metals, deposits

Fig. 3 Cyclic voltammograms for a rotating gold plated platinum-disc electrode in 1.0 M hydrochloric acid

Fig. 4 The effects of stirring and electrolyte temperature on the morphology of gold deposits produced at 700 Å/m² cathodic current density

obtained under diffusion-limited conditions are always rough or powdery. Thus, one would expect that any change of the experimental conditions leading to a higher amount of gold being deposited from bulk gold(I) would give rise to an increase in the roughness of the deposit. These changes should also be accompanied by an increased current efficiency, since a larger amount of gold is deposited by a given charge from gold(I) in terms of

than is deposited from gold(III) in terms of

Figure 4 shows that, as expected, increased temperature or stirring intensity leads to an increased contribution by reaction (5) with a higher current efficiency and at the same time an increase in deposit roughness. It was also shown in this investigation that a decrease in current yields rougher gold deposits. These trends are clearly contrary to those normally observed with other metals. However, it must be pointed out that under conditions where control by diffusion of the deposition from gold(III) becomes the overriding factor, an increase in temperature or stirring intensity or a decrease in current, will have the expected effect of reducing the roughness of the deposit.

The use of periodic current interruption or current reversal has often been advocated (7) and practised (8)

as a means for the attainment of smoother electrodeposits. It was found during the present investigation that a significant decrease in micro-roughness resulted from the application of pulsed currents (5) and the method was tested in the pilot-scale experiments to be described below.

Relation Between the Morphology and the Purity of Gold Deposits

Observations by the personnel of the Rand Refinery that higher purities had been attained under conditions which produced deposits of poor morphology, indicated that some laboratory testwork should be carried out with the aim of confirming that smooth deposits are not necessarily the purest.

As silver is invariably the major impurity in cathodic gold deposits, the silver content of a deposit is a reliable measure of its purity. The results of 20 test runs demonstrated quite clearly that the rough deposits have a lower silver content than the smooth. As already indicated, the cathodic gold deposits are expected to be rougher the higher the portion of the gold deposited from bulk gold(I). In other words, the roughness of a deposit should increase with the current efficiency calculated on the basis of a three-electron process (equation (6)). Thus, as the roughness of a deposit seems to be the decisive factor as far as contamination by silver is concerned, one would expect the silver content of a deposit to be a function of current efficiency. As Figure 5 shows, this is indeed the case. Although the data show some scat-

Fig. 5 Relationship between the current efficiency (or roughness) and the silver content of gold cathodes

ter, the silver content of the deposits is seen to decrease markedly as the current efficiency increases.

The average silver content of the 10 test deposits classified as smooth or very smooth was 171 ppm.

Four of these deposits were obtained in a stirred electrolyte and their average silver content was 249 ppm. This agrees with expectations because a stirred electrolyte contains more suspended silver chloride than one that is unstirred.

The above results can tentatively be explained by assuming that the suspended silver chloride is incorporated continuously into the cathode. The amount of this silver chloride that is accessible to the wash solution is presumably proportional to the surface area of the deposit. Accordingly, one would expect a gold deposit consisting of very fine needles to be purest after washing and this agrees with the result that the almost felt-like deposits of Figure 4c were found to contain the lowest amount of silver, as little as 0.5 ppm after washing. Photomicrographs (Figure 6) of the cross-sections of smooth and rough deposits illustrate the marked difference in morphology of the latter, and the variations which can arise in the ease of access of wash solutions to them.

In terms of plant practice, an important conclusion is that a compromise must be made between the desirability of dense deposits produced over a long plating cycle and, from the point of view of purity, of a certain amount of roughness in the deposits.

Pilot-Scale Experiments: Typical Results

The pilot-scale experiments were carried out in a porcelain cell of 20 litre capacity. The normal arrangement of the electrodes consisted of a cathode

a) Room temperature, no stirring

× 125

b) 50°C, no stirring

× 45

Fig. 6 Cross-sections of gold deposits produced at 700 A/m² cathodic current density

Fig. 7 Deposition at room temperature, 400 A/m² cathodic and anodic current density

Fig. 8 Deposition at 50°C, 850 A/m² cathodic and anodic current density

Fig. 9 Deposition at 50°C, 800 A/m² cathodic current density, 1600 A/m² anodic current density

Fig. 10 Deposition at 50°C, 850 A/m² net cathodic and anodic current density, pulsed current 100 ms on, 100 ms off

Typical gold deposits obtained during pilot-scale runs

and an anode on either side of the cathode. Thus, essentially the anodes were used on one side only, their active area being about 145 cm². They had the same composition as those used at the Refinery. For the cathode, either one or two cathode-starter sheets (99.99 per cent gold), with an immersed area of 300 cm² each, were used. The distance between the cathode and the anodes was 5 cm.

An electrolyte that had been used for some time at the plant and assayed 70 g/l of gold and 120 g/l of

hydrochloric acid was employed for these experiments. Agitation was by means of a laboratory stirrer. During runs at high temperature, the temperature was controlled at 50°C. During the runs carried out at room temperature (no control) the temperature rose typically from 20 to 25°C due to resistive heating of the electrolyte. The power supply could be programmed to deliver either direct current or rectangular current pulses of variable frequency. The duration of each run was 20 hours.

Some typical cathodes obtained are shown in Figures 7 to 10. All these cathodes were produced under fairly weak stirring (30 r/min). Figure 7 shows the principal features of the deposits made at room temperature. Whereas the lower three-quarters of this cathode were very smooth indeed, the top was powdery and rather bulky, and did not adhere well to the cathode. This is a common observation (6) and indicates the onset of diffusion-control under conditions of natural convection. The principle, already stated, that low temperature leads to the formation of smooth deposits is confirmed by Figure 7 and at the same time it is demonstrated that the maximum applicable current is fairly low at room temperature because the rate of diffusion is low. Although this could not be confirmed during these experiments, the silver content of such a deposit is expected to be rather high in view of the laboratory-scale experiments reported above and of experience gained at the plant.

Figures 8 to 10 show cathodes obtained at 50°C. The applied current density was about double that used at room temperature. Figure 8 shows a cathode that would be acceptable if it were not for the peculiar grape-like growth. This type of growth was always linked with low anodic current densities. Thus, when the anodic current density was doubled, the growth was no longer observed, as is evident from Figure 9. From what has been stated already, it is clear that the amount of gold fines formed decreases with increasing anodic current density.

It was observed during the pilot runs that at low anodic current density the fines agglomerated at the surface of the electrolyte. These agglomerates, about 1 cm in diameter, attached themselves to the top of the cathode and generated the characteristic growths shown in Figure 8.

In plant practice, the aim should certainly be to apply as high an anodic current density as possible, both to prevent the formation of the grape-like growths, and to minimise the amount of gold fines in the cell sludge.

Figure 10 shows the effect of current pulsing. In this experiment rectangular pulses of 100 ms duration interrupted by off-times of 100 ms were used. Comparison of Figure 10 with Figure 8 reveals two effects of current pulsing. The first is the absence of a grape-like growth, and the second is the production of a smoother deposit, which, however, showed a marked tendency to grow individual nodules. Whereas nodular growth is potentially detrimental because it can lead to shorting, a smooth deposit is not desirable in terms of deposit purity. Another important aspect is that the total current applicable at a smooth surface is considerably lower than that at a rough surface. Therefore, the production of a rough deposit permits

increase of the deposition current with time and makes an increase in production possible. It can thus be stated that the ideal cathodic gold deposit is one that is not so bulky or dendritic as to cause shorting, but is rough enough to allow high current flows and yield low silver contents.

Conclusions

Whereas the optimum conditions for the operation of an electrolytic gold plant cannot be derived directly from this investigation, the effects have been demonstrated that can be expected from changes in the variables involved. Thus, a high anodic current density will help to reduce the amount of gold fines formed. This will probably mean that the anodes must be smaller than the cathodes in the plant cells. The cathodic deposit should be rough because this is beneficial in terms both of plant performance and of purity of the cathodes. On the other hand, excessively bulky or dendritic deposits must be avoided and this can be achieved, at least in part, by the reduction of the amount of gold fines which, if too high, leads to undesirable growths on the cathodes. The use of periodic current pulsing or other forms of alternating current is not recommended.

The investigations reported here have resulted in a considerable advance in our understanding of the various reactions that occur in the electrolytic cells and a limited application of the findings has already produced significant practical improvements at Rand Refinery Ltd. Consistent production of gold of 99.99 per cent purity has been achieved and the quantity of gold fines produced in the cells has been reduced.

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