



Innovations in precious metal recovery

by C. van Tonder*† and M.J. Sole†

Paper written on project work carried out in partial fulfilment of B Tech (Engineering Metallurgy) degree

Synopsis

This investigation relates to a multi-purpose electrolytic system. Its primary purpose is to electrowin gold from high or low concentration gold cyanide solutions and/or from gold sludge, and to convert the recovered gold into a gold (alloy) electroform or electrode at the gold mine itself. These operations are carried out sequentially and *in situ* in the same electrolytic cell. Electrorefining of the gold recovered may also be done in the cell. The system applies to silver as well, and may be adaptable to base and platinum group metals. It could also be used in environmental applications, to remove undesirable metals present in aqueous solution at very low concentration. The work to be discussed forms part of recently filed patent applications. Subsequent and future developments of the system are briefly outlined.

This paper, in part or in full, has been published by the Metallurgical Mine Managers Association (MMMA), with permission from the authors.

Introduction

In large-scale gold mining operations the finely crushed ore is leached in sodium cyanide solution to yield a leach solution containing ~6 ppm gold. This solution is then treated with activated carbon to adsorb the gold. The loaded carbon is screened off and the adsorbed gold is then eluted with a hot caustic solution to yield a gold eluate containing ~600 ppm gold. The carbon is heated periodically to regenerate it for reuse later. The eluate then passes through electrowinning cells where the gold is deposited on to cathodes of knitted stainless steel wool. The loaded cathodes are removed from the electrowinning cells and manually washed using high-pressure water jets to dislodge a gold sludge. This is filtered, after which the filter cake is smelted and cast into impure* gold bars. These bars are sent to a refinery, generally at a remote location, for further purification. In recent times the

*The main impurity in South African gold ores is silver, with a small amount of copper also present.

electrowinning has also been carried out in so-called 'sludge reactors'¹, which allow the electrowinning and dislodgment steps to be carried out *in situ* and automatically. The product remains a gold sludge that is filtered and smelted as before. There is thus an incentive, not only to convert the eluate and/or the sludge to a value-added product, directly at the mine itself, but also to explore the possibilities of eliminating the carbon activation step. If a degree of gold refining could be achieved at the same time, this would be an added bonus.

In small-scale gold mining operations the product is often a gold gravity concentrate, which may be treated with mercury to recover the gold using amalgamation and mercury volatilization. In any event, the value of the product that can be sold is generally very low. Again, there is an incentive to add value to the product and possibly to refine it as well.

The aim of the present investigation was therefore to develop apparatus and procedures to try to meet the requirements outlined above. Patents^{2,3} have been granted covering the work reported here.

Experimental

Equipment

A flow diagram and the general arrangement of the equipment used are shown in Figure 1. The primary electrowinning (EW) tank and the electrowinning/electroforming (EWEF) cell, together with the electromagnetic pump and relevant pipe-work comprise the primary electrowinning circuit for gold eluate solutions from two South African gold mines. These

* University of Johannesburg

† Zenzele Technology Demonstration Centre, Randburg, South Africa.

© The South African Institute of Mining and Metallurgy, 2006. SA ISSN 0038-223X/3.00 + 0.00. Paper received Feb. 2006; revised paper received Mar. 2006.

Innovations in precious metal recovery

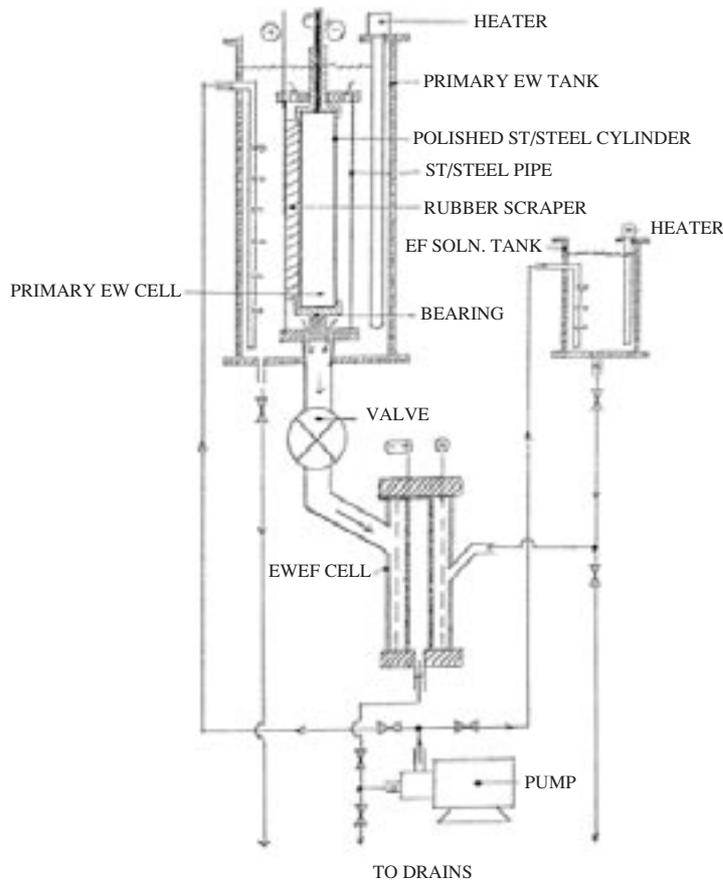


Figure 1—Flow diagram and general arrangement of equipment used to electrowin and electroform gold metal from gold eluate and gold sludge

eluates typically contain >600 ppm gold. Inside the primary tank is located one or more primary cylindrical EW cells (only one is shown), which plug into receptor discharge cone(s), as shown in Figure 1. Various designs of interchangeable EW cells have been investigated, but for this investigation the simplest one was chosen, the main consideration being to generate gold sludge easily and to transfer it to the EWEF cell. A thermostatically controlled heater provides for temperature control of the circulating solution.

The primary EW cell essentially consists of two coaxial stainless steel cylinders, where the outer one is the anode and the polished inner one is the cathode. The latter may be rotated periodically so that electrodeposited gold particles, which are loosely adherent to the cathode surface, are scraped off by means of a fixed rubber scraper, and drop downwards under gravity. The action of eluate circulation causes them to be further transported down into the EWEF cell. Here they are caught up on the high surface area (HSA) cathode of that cell, which acts as a filter (see Figures 2 and 3). Thus, the gold particles are in electrical contact with that electrode. Since secondary electrowinning may also be carried out simultaneously in that cell, the gold from both sources is effectively combined at the cathode.

However, initially the EWEF cell was used on its own to electrowin gold from original and diluted eluate solutions. These solutions were contained in the smaller electroforming (EF) solution tank (prior to filling the tank with the electro-

forming solution required for the electroforming tests). By appropriate valve manipulation, the solution could be recirculated through that system using the same magnetic drive pump as before (see Figure 1). A thermostatically controlled heater enables the temperature of the circulating solution to be kept at the required temperature.

The EWEF cell is shown in more detail in Figure 2. It is constructed of polypropylene and fitted with a large inlet port for gold eluate and/or sludge, and a smaller one for gold eluate (or electroforming) solution. It contains three electrodes. The axial one A is a polished, tapered, stainless steel or titanium rod, which acts as a mandrel during electroforming operations. It is fitted with jack-screws, as shown, so that after removal from the cell, the gold electroform may be removed mechanically. Clearly, other mandrel designs and materials could also be used. During electrowinning operations mandrel A may be made anodic or left uncharged.

Surrounding the mandrel is a cylindrical coaxial HSA electrode B. As shown in Figure 3, this comprises a porous polypropylene tube around which is wound, in the form of a 'Swiss roll', a combination of oxide-coated titanium or stainless steel wire-cloth and graphite felt. Two oxide-coated titanium or stainless steel strips provide the current connections, and cable ties serve to hold the system tightly together. During electrowinning this electrode is made cathodic and during electroforming (or electroplating) it is made anodic. Surrounding electrodes A and B is a third

Innovations in precious metal recovery

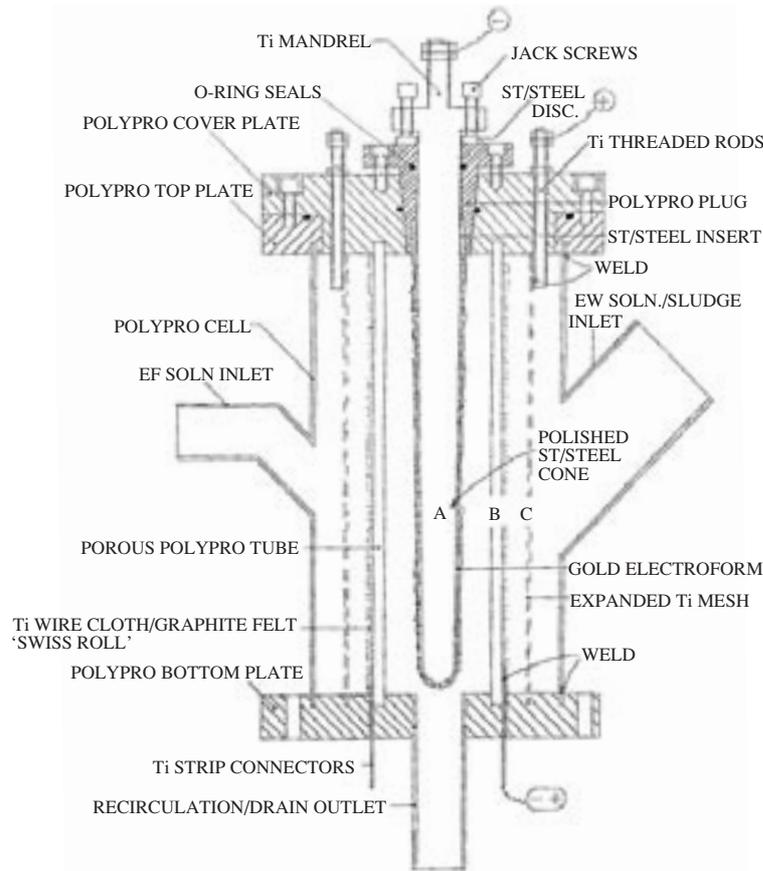


Figure 2—Schematic diagram of the EWEF Mark I Cell used to electrowin and electroform gold/silver alloy *in situ*

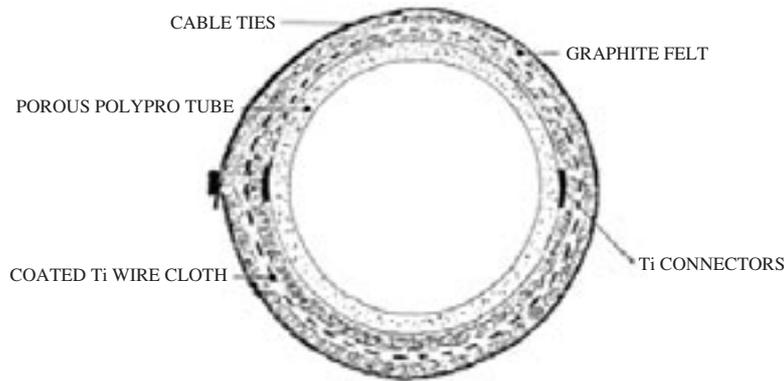


Figure 3—Detail cross-section of the high surface area (HSA) electrode used in the EWEF Mark I cell

electrode C, which acts as an anode during electrowinning and is uncharged during electroforming operations. It is a coaxial cylinder of expanded oxide-coated titanium or stainless steel mesh.

As indicated above, the EF tank may be used for both eluate solutions during electrowinning, or for an electroforming solution during electroforming. It is drained, of course between these operations. The electroforming solution used contained, typically, potassium cyanide (5–50g/l), potassium hydroxide (5–20 g/l), di-potassium hydrogen phosphate (5–20 g/l), and sometimes a brightening agent.

A 10 volt, 50 amp DC power supply was used during electrowinning, and a 30 volt, 3 amp (ave.) pulse power supply for the electroforming operations.

Procedures

Undiluted gold eluate/sludge

The (200 l) primary EW tank and the (2, 5 l) EWEF cell were filled with gold eluate solution, which was then recirculated through the system. The primary heater was switched on and the solution temperature was controlled at the desired

Innovations in precious metal recovery

temperature. DC power was supplied to both the primary EW cell and to the secondary EWEF cell, at cathode current densities of typically 0.1–0.3 amps/square decimeter, for periods of up to six hours. During this time solution samples were taken as a function of time and these were subsequently analysed for gold content. At the end of the electrowinning operation, the current and heater were switched off, and, with the solution still being circulated, the primary EW cathode was manually rotated, such that the gold adhering to its surface was scraped off by the stationary rubber scraper. The gold sludge produced was then washed downwards to be caught up on the outer surface of the HSA electrode. The EWEF cell was isolated and the barren solution in it was drained and returned to the primary EW tank.

The EF tank and the EWEF cell were then filled with electroforming solution. Using the same pump, this solution could be recirculated and heated for this second-stage electroforming operation, in the same manner as described above. Solution circulation was continued at temperature for a while, to allow some of the finely divided gold on the HSA electrode to dissolve in the high cyanide solution. (In some cases gold solution was added to bring the gold content of the overall electroforming solution up to about 0.5 g/l). The DC or pulsed current was then switched on, with electrode B now anodic, electrode C uncharged, and the central mandrel A cathodic. Electroforming was continued for up to three days, taking solution samples for analysis, as before. At such low gold concentrations electroforming kinetics is necessarily slow, but, as will be discussed later, it is believed that this problem can be overcome in large-scale (continuous) operations.

At the conclusion of electroforming the EWEF cell was drained, the mandrel A was removed from the cell, and the gold (alloy) electroform separated from the mandrel. The metallurgical characteristics of this electroform varied, depending upon the electrodeposition parameters used, but integral tapered cylinders or thimbles could be produced under optimum conditions.

Original and diluted eluate solutions

Important objectives in this case were to establish whether or not very dilute gold solutions, such as those obtaining in gold leach solutions (i.e. prior to the activated carbon gold concentration step) could, in principle, be treated directly, using EWEF cells of this type, as well as to compare the kinetics of gold extraction under different conditions.

Eluate solutions, at various dilutions, were treated in the smaller volume secondary system alone, using procedures analogous to those discussed above. Both electrowinning and electroforming of gold were found to be possible in the EWEF Mark I cell.

Gold electrorefining

Various approaches were tried to see whether the silver, the main impurity, could also be removed *in situ*, so that the main end product, gold metal, would be relatively pure. The simplest and best approach was to plate out the silver first, using direct current and a very low cathode current density.

In cyanide solution silver (and copper), having lower electrodeposition potentials than gold, are the more noble metals and will plate out preferentially. Thus, these impurities could be deposited on the mandrel A initially. When this process was complete, the mandrel could be removed from the cell and the silver removed from it, before replacing it in the cell. The electrodeposition parameters would then be optimized for gold electroforming.

An alternative approach would be first to electroplate the gold alloy on to a titanium rod, which would later be used as an anode in a conventional gold (chloride) electrorefining cell.

Results and discussion

Electrowinning of gold eluates

The results of using the EWEF Mark I cell to extract gold from various gold eluates from two South African gold mines (A and B) are given in Table I. The volume of solution used in each run was 18 litres. These results are also plotted graphically in Figures 4 and 5. Six successive runs were carried out, the first four (A) from eluate solutions from gold mine A, and the last two (B) from eluate solutions from gold mine B. Thus, the initial gold concentrations varied from ca. 100 ppm to ca. 900 ppm. Various other parameters were varied, including temperature, flow rate, and the cathode current density (expressed in terms of the geometric area of the HSA cathode, which was ca. 5 dm²).

Referring to Table I and Figure 4, it is evident that in all cases gold extraction is very effective, the residual gold concentration being reduced to less than 1 ppm, i.e. gold extractions of >99%, in times ranging from 1.5 to 4 hours.

In Figure 5 the logarithm of the residual gold concentration is plotted as a function of time. It is clear that in the region down to about 1 ppm gold a linear relationship applies. The times required to reach this value of gold concentration under the different conditions are readily defined by the intersections of the graphs with the abscissa.

Some other trends were observed:

- comparing runs 1 and 2, higher operational temperatures improved the kinetics of gold extraction and also meant a lower voltage requirement
- comparing runs 3 and 4, a higher cathode current density improved the kinetics of gold extraction, but with a higher voltage requirement, although the lower flow rate and temperature of run 4 would also have had some effect
- comparing runs 2, 6, and 5, it is evident that at the same temperature (ca. 44 C), flow-rate (32 l/min) and cathode current density (2A/dm²), the times to reduce the gold concentration to ca. 1 ppm gold are fairly similar, irrespective of the initial gold concentration
- in some cases (Runs 4 and 5) very long extraction times resulted in a small amount of gold going back into solution
- it may also be noted that the slopes of the graphs in Figure 5 are dependent upon the kinetics; the steeper the gradient, the faster the kinetics.

Innovations in precious metal recovery

Table 1
Gold extraction from gold eluates from two South African gold mines using the EWEF Mark I cell

Run	Elapsed time (min)	Residual gold (ppm)	Ave. temp. deg. C	Voltage (volts)	Current density (A/dm ²)	Flow Rate (l/min)
1 A	0	103	21	6.5	2	32
	5	91.5				
	10	82.2				
	15	78.5				
	30	56.6				
	60	36.7				
	120	14.8				
	240	1.05				
360	0.08					
2 A	0	103	43	4.2	2	32
	5	98.5				
	15	56.0				
	30	26.8				
	60	6.7				
	120	0.96				
	240	0.34				
3 A	0	349	43	4.8	4	32
	30	-				
	95	1.4				
	180	0.68				
	280	0.35				
4 A	0	342	34	3.8	2	16
	30	133				
	90	14.5				
	150	0.99				
	315	1.25				
5 B	0	895	44	3.8	2	32
	5	797				
	19	510				
	30	251				
	90	0.16				
	190	0.30				
	305	1.06				
6 B	0	164	45	4.5	2	32
	5	154				
	16	106				
	40	45.7				
	72	12.9				
	110	2.09				
	240	<0.01				

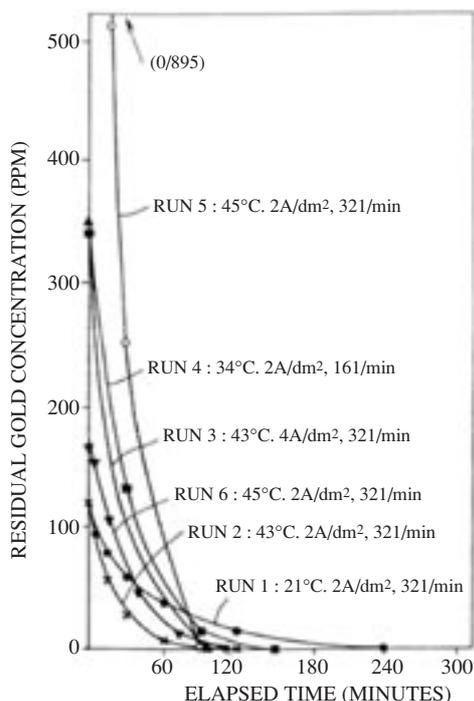


Figure 4—Graphs showing gold extraction from various eluate solutions as a function of time, using the EWEF Mark I cell for electrowinning

In later testwork, when using the larger 10 litre EWEF Mark III cell of similar design, the results shown in Figure 4, were confirmed, as is illustrated in Figure 6. These results show quite dramatically that gold solutions ranging in concentration from over 2 500 ppm, down to 20 ppm gold, can be treated in EWEF-type electrowinning cells.

It is evident, therefore, that high surface area graphite felt, which may have a typical specific surface area of > 260 m²/kg 4, is extremely effective in extracting gold from eluate solutions. Furthermore, according to Stavart *et al.* 4, 2000 kg of gold per m³ of felt can be loaded at 400 A/m² from dilute gold solutions (30 mg/l Au), with classic Faraday yields of 6–12%. Thus, the potential for employing such electrodes in gold hydrometallurgy is very significant.

In addition to the above, electrowinning tests runs were carried out in the primary electrowinning circuit (see Figure 1), where the intention was primarily to produce gold sludge. There was a transparent section in the discharge pipe leading to the EWEF Mark I cell, and so when the gold-loaded primary EW cathode was rotated, as described above, the gold sludge could be seen to be falling into the cell. This sludge would later be converted into gold electroforms (see below).

Innovations in precious metal recovery

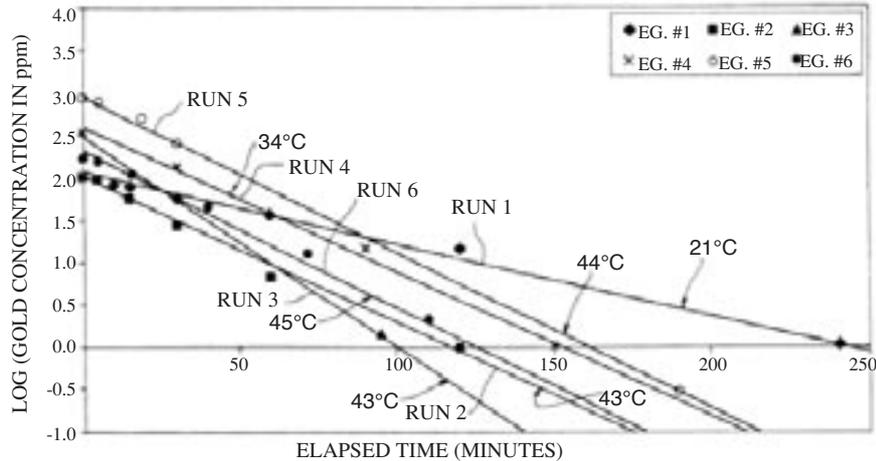


Figure 5—Plots of log (residual gold concentration) as a function of time, which provide an indication of gold extraction kinetics

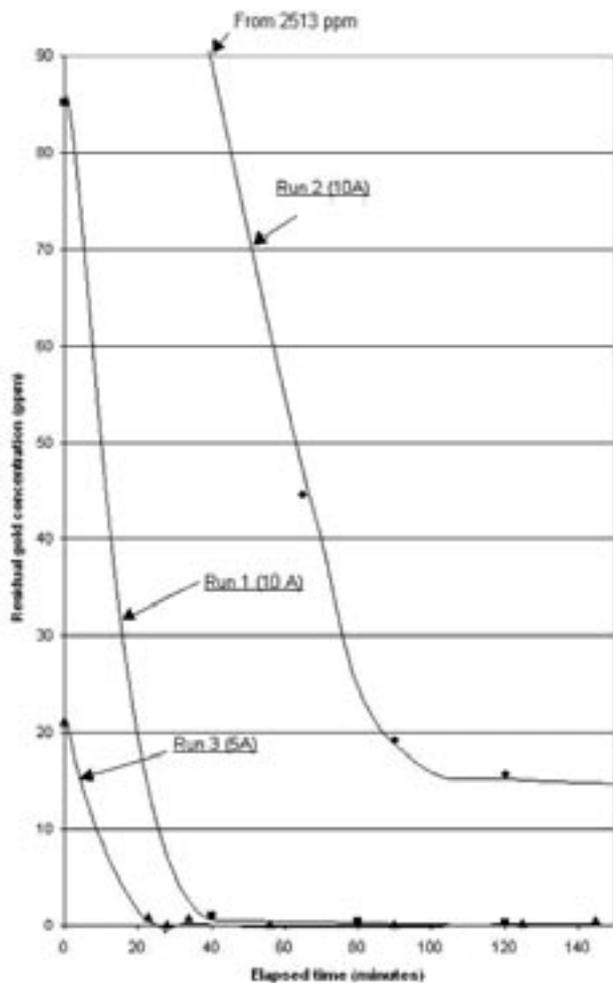


Figure 6—Graphs showing gold extraction from various solutions as a function of time, using the EWEF Mark III cell for electro-winning

Electroforming

Following the completion of the six electro-winning runs, calculation showed that there should have been about 30 grammes of gold on the HSA electrode. To this was added 2 grammes of particulate gold metal by entraining it in the re-

circulating solution, so that it would be trapped, as described above. As mentioned above, the aim was now to strip all the gold from electrode B, by making it anodic with respect to electrode A in Figure 2. Because of the limited amount of gold present, only part of electrode A was used to produce electroforms.

Ideally, the type of electroforming solution that should be used would contain a high concentration of gold (typically 8–40 g/l), and might contain proprietary additives to achieve a good integral fine-grained electrodeposit at relatively fast deposition rates. Because of the impracticability of using such a solution in the presence of such a small amount of electrowon gold—any effects would be swamped—the electroforming solution used was 18 litres of a gold eluate solution from mine B. At the start this contained *ca.* 200 ppm gold. To this solution was added sodium cyanide (10 g/l), dipotassium hydrogen phosphate (5 g/l), sodium hydroxide (5 g/l) and a proprietary brightener (5 ml/l).

Electroforming was carried out at 40–45 C, initially at *ca.* 0.15 A/dm², and later this was decreased to 0.1 A/dm². Finally, the current was changed from DC to a pulsed output, still at 0.1 A/dm². These changes were made in an effort to improve the quality of the electroform produced. This initially had appeared dark and rough, and possibly unsuitable to be removed from the mandrel as an integral electroform.

As the gold concentration of the electroforming solution was very low and very low currents were needed, this implied very long deposition times, and a really good deposit was hardly to be expected. Nevertheless, a good electroform was obtained at an average current density of 0.3 A/dm² under good pulse condition. The gold alloy electroform produced is shown in Figure 7.

Finally, when nearly all the gold had been removed from the total of 50 litres of gold eluate treated, it was found that the mass of gold recovered in the form of electroformed tapered tubes represented a gold recovery of *ca.* 95%.

In commercial practice, where gold is continually being extracted, and a gold mass of a kilogram, or more, is present on the HSA electrode, there would be no problem about having a high gold concentration electroforming electrolyte in

Innovations in precious metal recovery



Figure 7—Electroformed tapered tube of gold/silver alloy produced in the EWEF Mark I cell

circulation. In that case the cost of the circulating load of gold in the electroforming solution would not be prohibitive—in relation to the value of the gold recovered. Essentially, during the electroforming operation gold on the anode would dissolve, while gold in solution would not be consumed and would merely serve as a high-speed transport medium.

Recent developments

The experiments reported above were conducted in a laboratory-scale batch unit. This has subsequently been up-scaled to become a small pilot plant, having two EWEF (now designated EWEREF) cells of differing design, and with volumes of 50 and 100 litres, respectively (see Figure 8). Initial tests in the laboratory demonstrated that separate silver and gold electroforms could be produced in the EWEREF Mark IV cell. These are shown in Figure 9.

However, before all the intended tests could be completed, the opportunity arose to install this plant on a large gold mine. Here gold eluate (and sludge) would be readily available, initially on a batch basis, but eventually on a continuous basis, and there would be the opportunity to build up experience under realistic plant conditions.

Test work at the Kloof gold plant of Gold Fields Limited is currently in progress, and, as a result, improved cell and system designs, for which patent protection⁵ has been sought, are in the developmental stage. In addition, certain laboratory tests have shown that the kinetics of gold electroforming can be increased by an order of magnitude, or more,



Figure 8—Small-scale gold recovery pilot plant, showing the 400 l reservoir and the EWEREF Mark IV and Mark VI cells

Innovations in precious metal recovery



Figure 9—Gold, silver and gold/silver alloy electroforms produced in the EWEF Mark IV cell

yet still yielding good integral electroforms of hard gold. These unusual synergistic techniques have also been incorporated into the latest cell designs, and patent applications.

It is the intention to design cathode mandrels, such that various up-graded pure gold (~99.5%) products can be produced from gold eluate/sludge *in situ* and at the mine location. These products might include gold plates, gold foil and hard (~140 VPN) gold jewellery⁷. It is perhaps too early to speculate, but we believe that it will eventually be possible to do the same, using gold leach solution (~6 ppm gold) as the starting material. If this proves to be viable, it could revolutionize the gold mining industry.

Conclusions

The following conclusions may be drawn from the investigations reported here:

- Gold, silver, and gold/silver alloy electroforms can be produced *in situ* in specially designed electrochemical cells, directly from gold cyanide eluates and gold sludge originating from South African (and other) gold mines. There is the further possibility of doing the same with the corresponding low concentration gold cyanide leach solutions
- The potential exists to utilize this type of *in situ* electroforming to manufacture value-added precious metal products in the form of plates, tubes, foil, jewellery, etc. at the mine itself, either as a niche operation on a large gold mine, or as a complete system on a small gold mine
- Electrorefining of gold and silver can be included in the operational sequence at the mine, thereby eliminating filtration of sludge, smelting, and gold refining elsewhere
- If the process features outlined can be fully commercialized, it will be possible to eliminate a number of steps in the production chain from gold ore to end-products, thereby reducing costs and enhancing profitability
- In principle, operations could be fully automated in order to minimize the possibility of gold theft.

Acknowledgements

This work was carried out under the auspices of Zenzele Technology Demonstration Centre, and the authors wish to thank most sincerely the centre manager, Dr Colin Logan, without whose enthusiastic support this project would not have been possible. Thanks are also due to AngloGold Ashanti for providing gold eluate solution, and to Allen Philips, consulting metallurgist to Gold Fields, who not only arranged for the supply of similar solutions, but also made possible the installation of our pilot plant at their Kloof gold plant. The helpful cooperation of staff at the Kloof plant is also gratefully acknowledged. Phil Vokes of C. I. Engineering made valuable contributions equipment design, manufacture and maintenance, and his services are most appreciated. This paper was first published in Circular No. 2, November 2005, Mine Metallurgical Managers Association. Permission was granted for this paper to be published in this edition of the *Journal*.

About the authors

Michael J. Sole, C.E.F., has been a member of the American Electroplaters' and Surface Finishers' Society (AESF) for over 25 years, and has specialised in the electroforming of gold and base metals. He holds a masters degree in Physical Chemistry from Rhodes University, Grahamstown, South Africa, and a Ph.D. in Chemical Physics from the University of Cambridge, Cambridge, England, where he also held an International Atomic Energy Agency Fellowship. He is the author of numerous scientific papers and several patents. He was the keynote speaker at the AESF Symposium on Electroforming, Las Vegas, USA, and guest speaker at the World Gold Council's 1st Symposium on Gold Jewellery Technology in Vicenza, Italy. He is semi-retired and works as electrochemical consultant at Zenzele Technology Demonstration Centre, in Randburg, South Africa.

Carl van Tonder holds a diploma in Physical Metallurgy from the Pretoria Technikon, South Africa, and is currently working towards a bachelors degree in Physical Metallurgy at the University of Johannesburg. His previous experience includes gold jewellery electroforming under Dr Sole at Huddy Diamond, and process development in precious metals at Rand Refinery and at Johnson Matthey in Johannesburg. He is currently employed as a technician at Zenzele Technology Demonstration Centre.

References

1. CARTNER, W.N. South African Patent Application No. 9811751, 'Electrowinning Cell', lodged 22 December 1998.
2. SOLE, M.J. South African Patent No. 2002/6170, 'Removal of Metals from Solution', granted 31 December 2003.
3. SOLE, M.J. South African Patent No. 2005/0298, Metals Recovery System—EMD Mark III, filed 12 January 2005.
4. STAVART, A., LEROY, C., and VAN LIERDE, A. Potential Use of Carbon Felt in Gold Hydrometallurgy. *Minerals Engineering*, vol. 12, no. 5, 1999. pp. 545–558.
5. SOLE, M.J. South African Patent Application No. 2005/02020 ElectroWinning, ElectroRefining and ElectroForming System for Gold Recovery, filed 10 March 2005.
6. SOLE, M.J. South African Patent Application No. 2004/3697, Gold Foil Manufacture, filed 14 May 2004.
7. SOLE, M.J. South African Patent No. 2005/01154, Electro Deposition' filed 9 February 2005. u