

# A modern study of the kinetics and mechanism of the cementation of gold

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## SYNOPSIS

A detailed fundamental study has been made of the various factors that influence the partial reactions comprising the electrochemical model of the cementation of gold from cyanide solutions by zinc. The effects of cyanide concentration, pH, agitation, additions of lead, and the presence of various impurity ions on both the anodic dissolution of zinc and the cathodic reduction of gold have been investigated. The results are used to explain the influence of these variables on the rate of cementation, and possible implications of this work for plant practice are discussed.

## SAMEVATTING

Daar is 'n gedetailleerde fundamentele studie gemaak van die verskillende faktore wat die gedeeltelike reaksies waaruit die elektrochemiese model van die sementering van goud uit sianiedoplossings deur sink bestaan, beïnvloed. Die uitwerking van die sianiedkonsentrasie, die pH, roering, loodbyvoegings en die aanwesigheid van ione van verskillende onsuiverhede op sowel die anodiese oplossing van sink as die katodiese reduksie van goud is ondersoek. Die resultate is gebruik om die invloed van hierdie veranderlikes op die sementeertempo te verklaar en moontlike implikasies van hierdie werk vir aanlegpraktyk word bespreek.

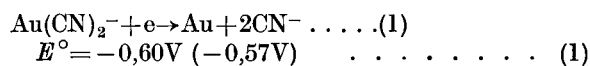
## Introduction

It is now almost a hundred years since the use of zinc for the recovery of gold from cyanide solutions was patented, and almost as long since the introduction of the process, using zinc shavings, on the Witwatersrand in 1890. Various improvements such as the use of zinc dust, the addition of lead nitrate, and the de-aeration of the pregnant solutions have resulted in precipitation recoveries of more than 99 per cent. When it is considered that this efficiency is obtained at gold concentrations down to 0,01 p.p.m., i.e.  $5 \times 10^{-8}$  mol/l, this is truly a remarkable process. It is even more remarkable when it is realized that the details of the mechanisms of the reactions taking place during cementation, and the role of various species in solution in promoting or inhibiting the recovery of gold, have received little attention and are still generally unclear. An excellent review of the chemistry of the process was published by Finkelstein<sup>1</sup> in 1972.

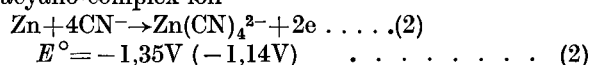
Despite the generally efficient operation of the precipitation plants, occasional (and often undetected) problems are experienced in reduction plants throughout the industry. In order to provide a sound theoretical basis for the operation and control of the reactions taking place during precipitation, the National Institute for Metallurgy (NIM) has undertaken an extensive fundamental study of the cementation of gold on zinc, and this paper outlines some of the results of this investigation. Further work in progress is aimed at the application to plant operation of the methods and ideas generated during the first phase.

## Electrochemical Model

It has long been recognized that the precipitation of a noble metal by a less-noble metal is electrochemical in nature. In terms of this mechanism for the precipitation of gold by zinc from cyanide solution, cathodic reduction of the dicyanogold(I) complex ion



is coupled to the anodic dissolution of the zinc as the tetracyano-complex ion



by transfer of electrons through the metal. A simplified schematic diagram of the precipitation reaction in terms of this electrochemical model is given in Fig. 1(a).

The standard reduction potentials for these two reactions are shown next to the above equations. A typical pregnant solution will contain 5 p.p.m. of gold ( $2,5 \times 10^{-5}$  M), 60 p.p.m. of zinc ( $10^{-3}$  M), and 0,02 per cent free cyanide as KCN ( $3 \times 10^{-3}$  M). The calculated equilibrium potentials for the two half-reactions under these conditions are given in parentheses. It is obvious that there is no thermodynamic restriction to the completion of precipitation since the difference in equilibrium potentials exceeds 0,5V. Inefficient precipitation cannot therefore be attributed to a lack of driving force, and extrathermodynamic considerations such as kinetics and physical factors must be invoked. This paper is concerned primarily with a discussion of the kinetics of the overall reaction that, as has been demonstrated above, can be divided into two separate electrochemical reactions each of which can be studied independently.

The kinetics of electrode processes are generally and conveniently described in terms of the variation with electrochemical potential of the rates of the reduction (cathodic) or oxidation (anodic) reactions, which, by Faraday's Laws, are directly related to the current. The experimental measurement of the current as a function of potential is fundamental to any electrochemical kinetic study, and the results are normally plotted as curves of current versus potential. Current-potential curves that could be expected for reactions (1) and (2) in a cyanide solution containing gold are shown in schematic form in Fig. 1(b). The convention by which anodic currents are assigned positive values and cathodic currents negative values should be noted. The form of the curves are discussed in detail below. However, the situation in

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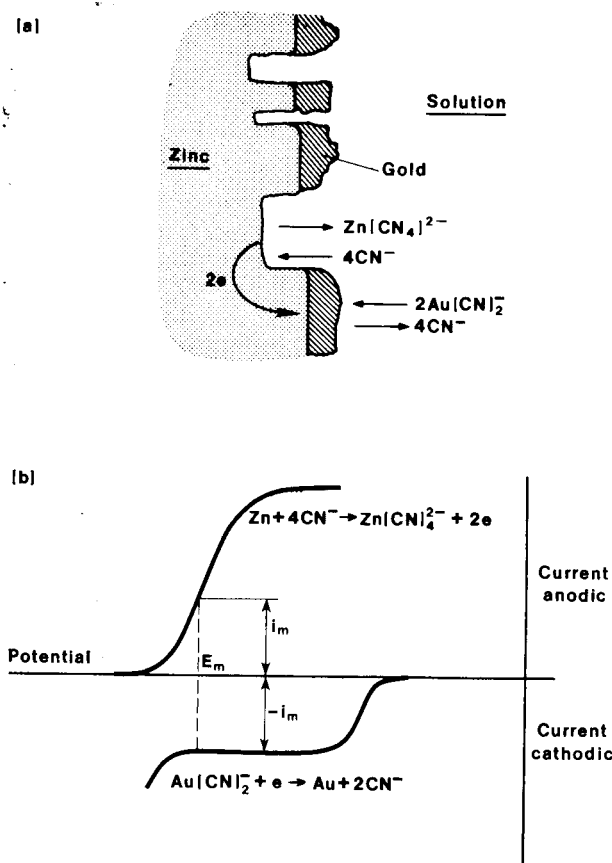


Fig. 1. (a) A simplified picture of the electrochemical model for the cementation of gold onto zinc  
 (b) Schematic current-potential curves for the anodic dissolution of zinc and the cathodic reduction of gold in a cyanide solution

which a zinc electrode is placed in a pregnant gold solution should be considered. Cementation of the gold will occur on the surface of the electrode at a rate that is determined by the condition that the rate (or current) of the anodic reaction must be equal but opposite to that of the cathodic reaction. This condition is satisfied at the potential  $E_m$ , the mixed potential, at which the rate is equivalent to a current  $i_m$ . It is not difficult to see that a change in either or both of the curves can result in a shift in the mixed potential with a resulting possible change in the rate of precipitation. A full understanding of the overall process therefore requires detailed information on the factors that influence each of the half-reactions. This aspect is presented in some detail in the following sections.

Finally, the results of well-controlled cementation experiments are described and the observations explained on the basis of the electrochemical model.

### Experimental Methods

All experiments were carried out using rotating-disc electrodes of spectrographically pure materials imbedded in PTFE holders that could be rotated at various speeds. These electrodes were used in a conventional three-electrode configuration with a platinum counter, and with

reference electrodes of either calomel or mercurous sulphate. However, all the potentials are quoted with respect to the normal hydrogen electrode.

The cementation experiments were conducted with a vitreous graphite-disc electrode that had been electroplated with a thin coating of zinc. After cementation for a fixed period (normally one hour), the residual zinc and precipitated gold were dissolved direct from the graphite surface by a small volume of aqua regia, and the resulting solution was analysed for gold by atomic-absorption spectrophotometry. At low concentrations of gold, it was necessary to use small volumes of aqua regia (typically 0,2 ml) and carbon-rod atomization to achieve suitable sensitivity, whereas conventional flame methods with larger volumes (3,0 ml) were used at high concentrations (2 to 5 p.p.m.). The potential of the disc was monitored during cementation. Unless stated otherwise, the cementing solution contained 0,01 M sodium cyanide and 0,02 M sodium chloride at a pH of 10,8.

All the experiments were carried out at room temperature ( $21 \pm 1^\circ\text{C}$ ), and all the solutions were made up with high-purity water from a Millipore purification system. Nitrogen gas was bubbled through all the solutions continuously.

### Anodic Dissolution of Zinc

The current-potential curve obtained at a rotating zinc-disc electrode in a solution containing 0,005 M  $\text{Ca}(\text{OH})_2$  (0,028 per cent CaO) is shown as curve (a) in Fig. 2. It is apparent that anodic dissolution does not occur at any appreciable rate in this solution. However, the addition of 0,005 M NaCN (0,033 per cent KCN) results in significant increases in the dissolution rate, shown by curves (b) and (c), that reaches a maximum value at potentials close to  $-0,8$  V and then decreases owing to passivation of the electrode by zinc hydroxide. The current at the peak is approximately proportional to the square root of the disc-rotation speed as expected for a diffusion-controlled process at a rotating-disc electrode. The current in the region of the peaks increases with increasing cyanide concentration and is therefore controlled by the mass transport of cyanide ions to the electrode surface. At pH values above about 11,0, the peak current also increases with increasing pH and this is due to the formation of soluble zinc-hydroxy complexes,  $\text{Zn}(\text{OH})_4^{2-}$ , and possibly to mixed hydroxy-cyanide complexes.

As cementation normally takes place at potentials in the range  $-1,2$  to  $-1,0$  V, the anodic behaviour of zinc in this region was studied in more detail. As expected, increasing cyanide concentration at constant pH resulted in a significant cathodic shift of the anodic dissolution curves (Fig. 3). A similar effect was noted when the pH value was increased at a constant cyanide concentration (Fig. 4). This is due, as suggested above, to the participation of hydroxyl ions in the rate-determining step of the dissolution reaction. The significance of these shifts of potential on the rate of cementation is discussed later.

The effect of precipitated gold and lead on the anodic dissolution of zinc is shown in Fig. 5, from which it can be seen that the presence of gold on the surface of the

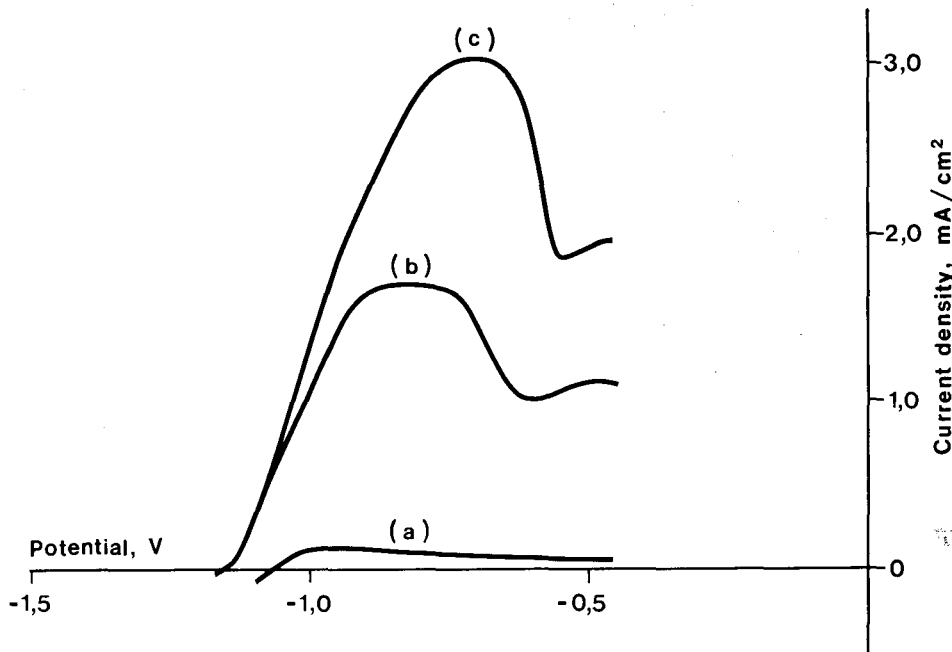


Fig. 2—Current-potential curves for the anodic dissolution of a rotating zinc-disc electrode in (a) 0,005M  $\text{Ca}(\text{OH})_2$  solution at 1000 r/min, (b) 0,005M  $\text{Ca}(\text{OH})_2$  and 0,005M NaCN solution at 250 r/min, and (c) at 1000 r/min

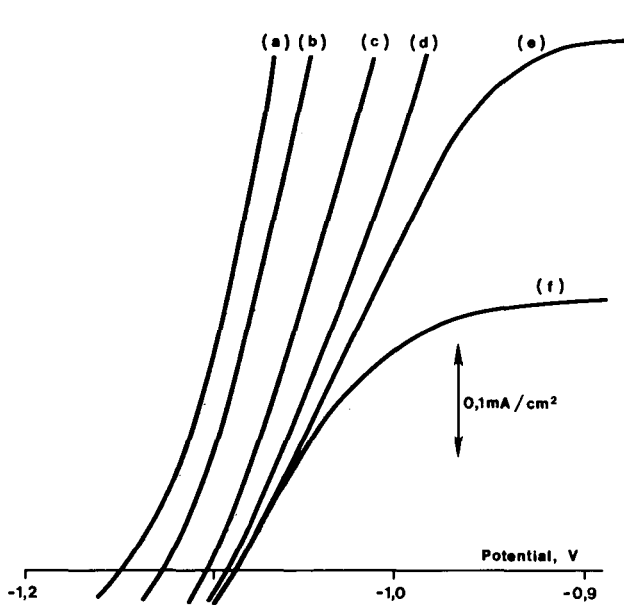


Fig. 3—Current-potential curves for the anodic dissolution of a rotating (1000 r/min) zinc-disc electrode in (a)  $2 \times 10^{-2}\text{M}$  (b)  $10^{-2}\text{M}$  (c)  $4 \times 10^{-3}\text{M}$  (d)  $2 \times 10^{-3}\text{M}$  (e)  $10^{-3}\text{M}$  solutions containing  $10^{-2}\text{M}$  NaCl at pH 11,0. The conditions for curve (f) are the same as for (e) except that the rotation rate was 250 r/min

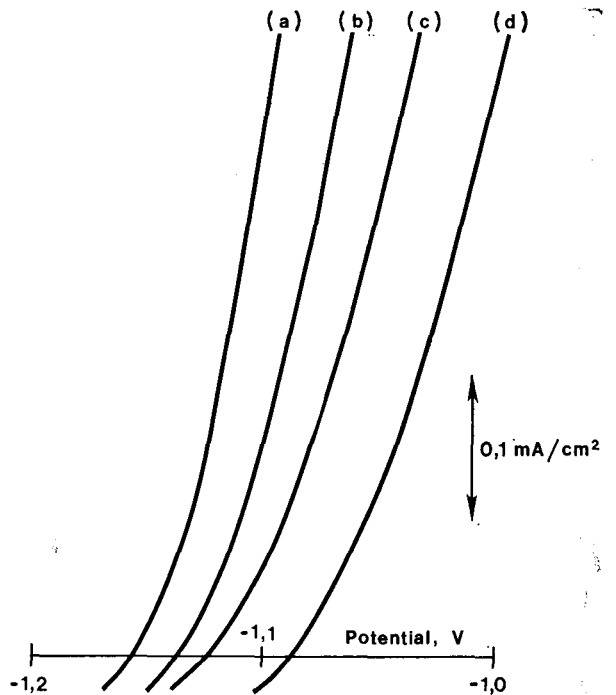


Fig. 4—Current-potential curves for the anodic dissolution of a rotating (1000 r/min) zinc-disc electrode in a solution containing 0,01 M NaCl and 0,01 M NaCN at pH values of (a) 12,0 (b) 11,4 (c) 10,7 and (d) 9,5

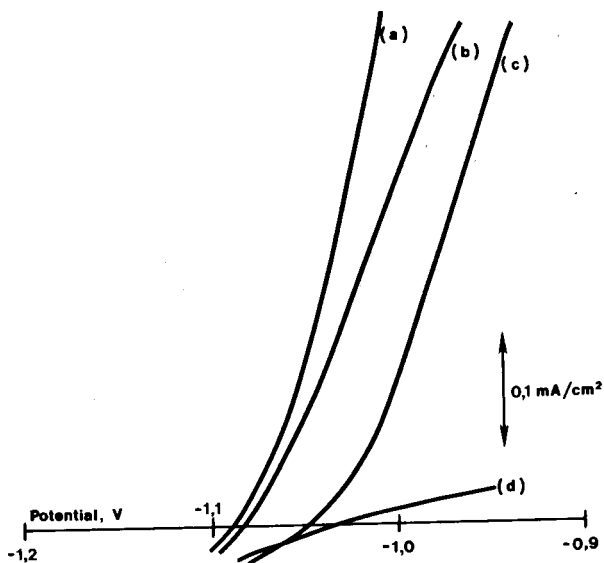


Fig. 5—Current-potential curves for the anodic dissolution of a rotating (1000 r/min) zinc-disc electrode in (a) a solution containing 0,01 M NaCl and 0,01 M NaCN at pH 10,8 (b) the same solution as (a) with 6 p.p.m. of gold after 90 minutes of cementation (c) the same solution as (a) with 6 p.p.m. of lead after 15 minutes of cementation (d) the same solution as (a) with 20 p.p.m. of sulphide

zinc has very little effect on the dissolution of the zinc even after cementation for 90 minutes. Lead, however, has a considerable retarding effect on the dissolution of zinc after cementation for only 15 minutes. This is probably due to the formation of a lead-zinc alloy on the surface rather than physical blocking of the zinc surface by the precipitated lead. This conclusion is based on the observation that the equilibrium potential (the potential at zero current) increases by about 0,03 V after the cementation of lead, which would be expected if the zinc surface were alloyed. The addition of sulphide ion resulted in immediate, almost complete, passivation of the dissolution of the zinc (Fig. 5) owing to the formation of an inert layer of zinc sulphide.

#### Cathodic Deposition of Gold

The current-potential curve obtained at a rotating gold-disc electrode in a cyanide solution is shown as curve (a) in Fig. 6. The cathodic current at potentials below  $-1,0$  V is due to the reduction of water to hydrogen, and the anodic current at potentials above  $-0,4$  V is due to the dissolution of gold as the aurocyanide ion. The addition of aurocyanide to the solution resulted in curve (b), which displays cathodic currents at potentials below  $-0,5$  V owing to the reduction of aurocyanide to gold metal (Reaction 1). The rate of reduction increases with decreasing potential until it becomes controlled by mass transport of the gold to the surface at potentials close to  $-1,0$  V and finally merges with the wave due to hydrogen evolution. The addition of as little as  $1,6 \times 10^{-5}$  M (3 p.p.m.) lead nitrate results in a significant anodic shift of about 0,2 V of the curve, i.e. the reduction of aurocyanide is considerably enhanced by the presence of lead in the solution. Also significant is the increased rate of the anodic-dissolution reaction in

the presence of lead. The deposition of gold becomes mass-transport controlled (independent of potential) at potentials below about  $-0,75$  V, as confirmed by a comparison of the observed limiting-current density ( $1,05$  mA/cm<sup>2</sup>) with that calculated from the Levich equation<sup>2</sup> for mass transport to a rotating disc. Similar depolarizing effects on the deposition and dissolution of gold were observed in the presence of thallium and mercury ions. The mechanism by which these metal ions act is still subject to considerable controversy and speculation<sup>3</sup>. It is suggested here that these metals, when co-deposited with gold, act by inhibiting the passivation of the gold surface by adsorbed AuCN (an intermediate in the deposition and dissolution of gold)<sup>3</sup>.

Current-potential curves for the deposition of gold from solutions of various cyanide concentrations in the presence of lead at constant pH are shown in Fig. 7. It is apparent that reduction is facilitated by low cyanide concentrations, with the anodic shift of about 0,1 V with each decade of decreasing cyanide concentration. This is as expected for reversible one-electron reduction of a complex containing two cyanide ions (theoretical shift 0,12 V per decade). The influence of pH at constant cyanide concentration on the deposition of gold in the presence of lead is shown in Fig. 8, from which it can be seen that pH has no noticeable effect on the rate of deposition in the range pH 10 to 12. Similarly, the addition of 5 p.p.m. of sulphide ion had no noticeable effect on the current-potential curves for the reduction of aurocyanide ion.

An important aspect of the deposition of gold is its

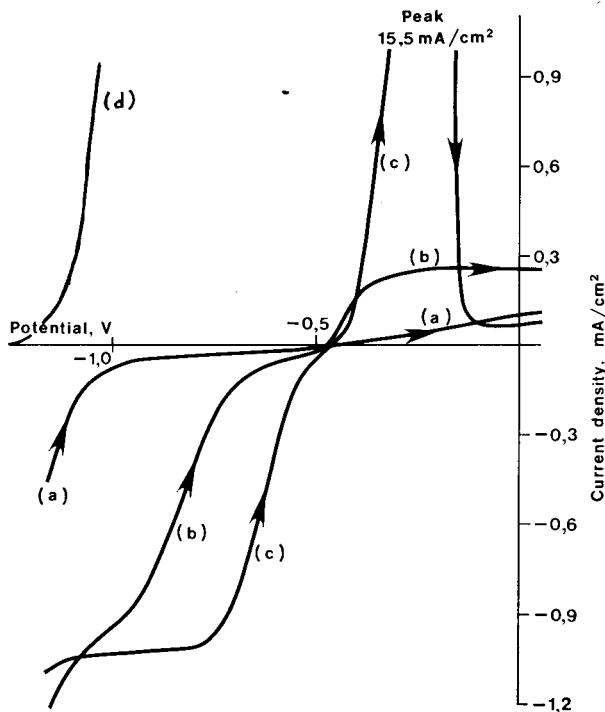


Fig. 6—Deposition of gold from a solution containing 0,005 M NaCN and 0,005 M Ca(OH)<sub>2</sub> onto a rotating (1000 r/min) gold-disc electrode. (a) No gold in solution (b)  $1,6 \times 10^{-5}$  M gold (c)  $1,6 \times 10^{-5}$  M lead. Also shown is (d), the curve for the anodic dissolution of zinc under similar conditions.

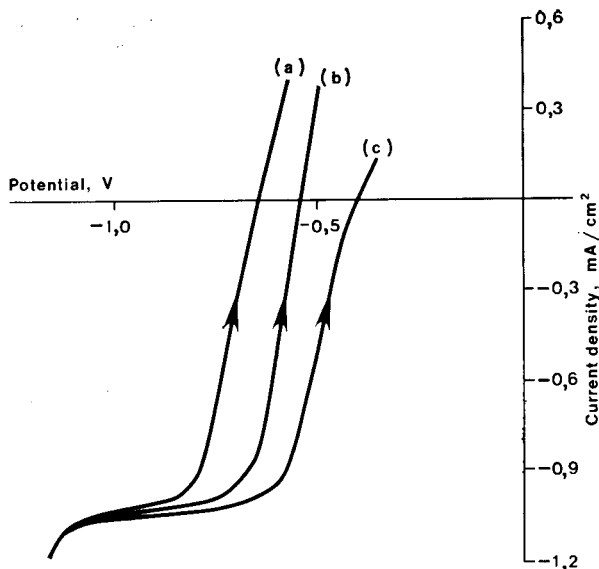


Fig. 7—Effect of cyanide concentration on the current-potential curves for the deposition of gold from a solution containing  $1,6 \times 10^{-3}$  M gold and  $1,6 \times 10^{-5}$  M lead at pH 11,2 onto a rotating (1000 r/min) gold-disc electrode (a) 0,1 M NaCN (b) 0,01 M NaCN and 0,09 M NaCl (c) 0,001 M NaCN and 0,1 M NaCl

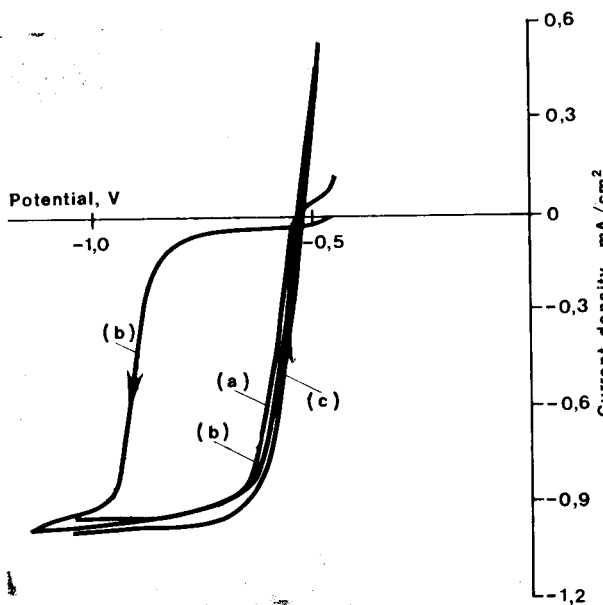


Fig. 8—Effect of pH on the current-potential curves for the deposition of gold from a solution containing 0,01 M NaCN, 0,09 M NaCl,  $1,6 \times 10^{-3}$  M gold, and  $1,6 \times 10^{-3}$  M lead onto a rotating (1000 r/min) gold disc electrode at (a) pH 12,0 (b) pH 11,0 (c) pH 10,0

sensitivity to the nature of the substrate. This is illustrated by the considerable hysteresis between the negative-going and positive-going sweeps shown by curve (b) in Fig. 8. No such hysteresis is observed in pure gold solutions. The origin of this effect is apparent when it is noted that gold will cement lead, and that a gold surface will, if held at potentials as negative as  $-0,5$  V in a lead-containing solution, become coated with lead. The deposition of gold onto a rotating lead-disc electrode is shown in Fig. 9. Attention is drawn to the first negative-going sweep, which shows that the deposition of gold

begins only at potentials below  $-1,2$  V but, after deposition of a gold layer, the positive-going sweep has the expected form for deposition onto a gold surface. A subsequent cathodic sweep is also shown that emphasizes the shift of about 0,4 V between deposition on gold and lead surfaces. A similar but less well-defined effect of overpotential deposition of gold onto a zinc surface was observed.

It is interesting to compare the deposition characteristics of gold with those of silver under similar conditions. This is demonstrated by the curves in Fig. 10, which show that (1) deposition of silver occurs at potentials that are about 0,3 V more anodic than those required for the deposition of gold, and (2) the addition of small amounts of lead has a beneficial effect on the deposition of gold that is similar, but less pronounced, to that on the deposition of gold.

### Cementation of Gold

The rate of cementation of gold onto a rotating vitreous-graphite disc plated with zinc is shown as a function of the concentration of gold in solution in Fig.

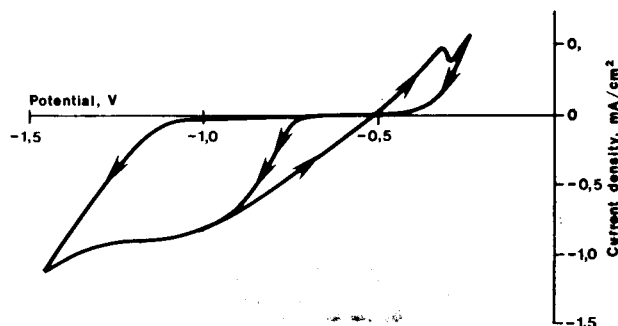


Fig. 9—Current-potential curves for the deposition of gold from a solution containing 0,02 M NaCl, 0,005 M NaCN, and  $1,6 \times 10^{-3}$  M aurocyanide at pH 11,0 onto a rotating (1000 r/min) lead-disc electrode. The first potential sweep ( $\rightarrow$ ) was initiated in a negative direction from  $-0,5$  V.

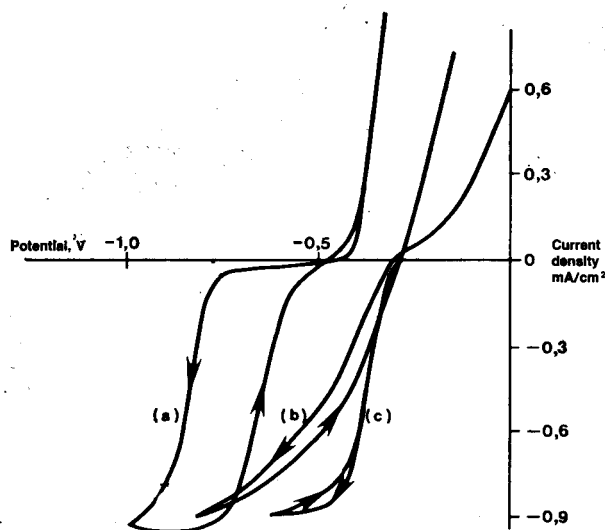


Fig. 10—Current-potential curves for the deposition of gold and silver onto a rotating (1000 r/min) gold-disc electrode from a solution containing 0,005 M  $\text{Ca}(\text{OH})_2$ , 0,005 M NaCN, and (a)  $1,6 \times 10^{-3}$  M gold and  $2 \times 10^{-5}$  M lead (b)  $1,6 \times 10^{-3}$  M silver (c)  $1,6 \times 10^{-3}$  M silver and  $2 \times 10^{-5}$  M lead

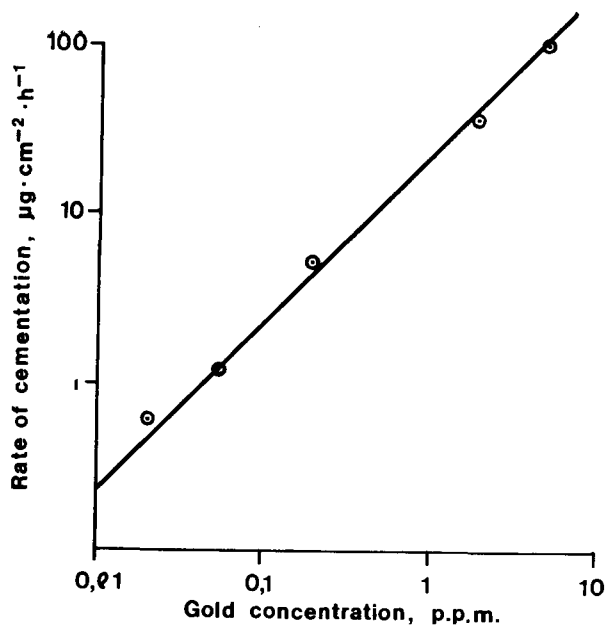


Fig. 11—Rate of cementation of gold from a solution containing 0.01 M NaCN, 0.02 M NaCl, and various amounts of gold onto a rotating (1000 r/min) zinc-plated graphite disc as a function of the concentration of gold in solution. The straight line is that calculated from the Levich equation for the rate of mass-transport to a rotating disc (diffusion coefficient of aurocyanide ion  $1.0 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ )

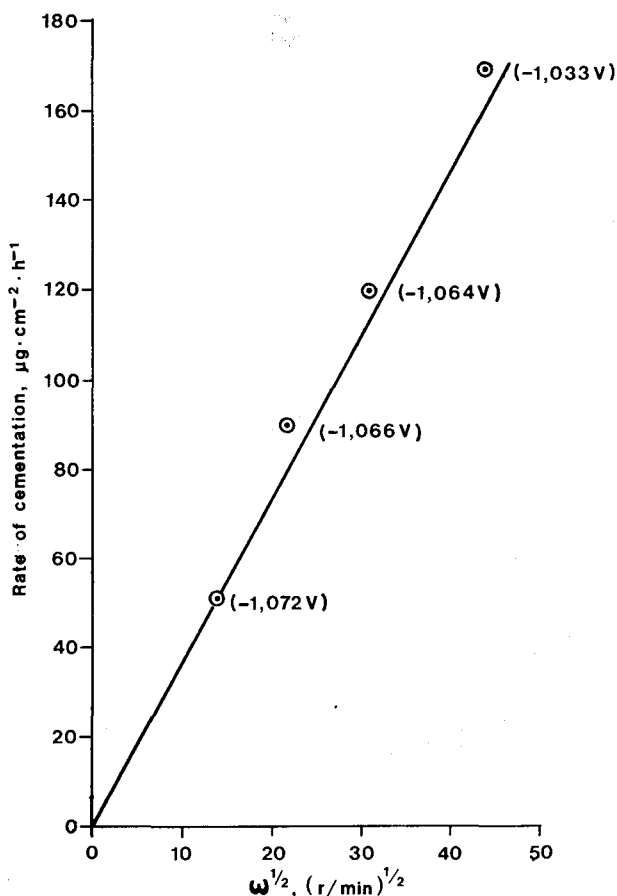


Fig. 12—Rate of cementation of gold from a solution containing 0.01 M NaCN, 0.02 M NaCl, and 5 p.p.m. of gold onto a rotating zinc-plated graphite disc as a function of the square root of the rotation speed of the disc. The straight line is calculated from the Levich equation as in Fig. 11. The figures in parentheses are the potentials measured during cementation

11. The solid line is that calculated on the assumption that the rate of cementation is controlled by mass transport of the aurocyanide ion (diffusion coefficient  $1.0 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ ) to the surface of the zinc disc. The excellent agreement of the observed rates with the theoretical values over a 250-fold range of gold concentrations confirms that, under these conditions, which approximate to those on the plant, the precipitation reaction is mass-transport controlled. Confirmatory evidence is given in Fig. 12, in which the rate of cementation of a solution containing 5 p.p.m. of gold is shown as a function of the square root of the rotation speed of the disc. The square-root dependence follows from the Levich equation<sup>2</sup>, which describes the rate of mass transport to a rotating disc. Once again, the excellent correlation with the theoretical values (shown as a solid line) confirms the nature of the rate-limiting step. Also shown in parentheses at each point in Fig. 12 are the potentials of the rotating disc measured during cementation. A comparison of these potentials with the curves for reduction of aurocyanide in Figs. 7 and 8 shows that cementation is, as demonstrated above, occurring in the diffusion-controlled region for the reduction of gold. Furthermore, the small but consistent positive shift of the mixed potential with increasing agitation is explicable in terms of the model shown in Fig. 1(b), in terms of which an increased rate of cathodic reaction (which includes reduction of residual oxygen) requires a corresponding increase in the rate of the anodic dissolution of zinc.

Table I gives the results of some of the experiments in which the effects were studied of changes in pH value and cyanide concentration of the solution on the rate of cementation. A variation in the pH value of the solution in the range pH 9 to 12 had no noticeable effect on the rate of cementation from solutions containing either 5 or 0.05 p.p.m. of gold. The mixed potential decreased from  $-1.014 \text{ V}$  at pH 8.9 to  $-1.137 \text{ V}$  at pH 11.9 during cementation in a solution containing 5 p.p.m. of aurocyanide, 0.02 M sodium chloride, and 0.01 M sodium cyanide. This shift in potential is consistent with the results shown in Figs. 4 and 8, which demonstrate that only the process of zinc dissolution is affected by changes in pH, as indicated by the cathodic shift with increasing pH. Similarly, the rate was independent of the cyanide concentration above about 0.002 M (0.013 per cent KCN). The decrease in rate at lower concentrations was accompanied by a considerable positive shift of the potential during cementation. Comparison of these potentials with the curves in Fig. 3 shows that the reduced rates are associated with the dissolution of zinc under conditions in which the rate is controlled by the diffusion of free cyanide to the zinc surface. This effect can be expected to be more pronounced if a heavy gold deposit is formed on the surface of the zinc, thereby restricting the diffusion to within the open pores of the deposit. In the extreme case, passivation of the zinc surface by zinc hydroxide is possible, as was suggested above as an explanation of the passivation hump shown in Fig. 2.

The effects of various anions containing sulphur on the rate of cementation are summarized in Table II,

TABLE I

THE EFFECT OF VARIATIONS IN pH AND CYANIDE CONCENTRATION

[Au] p.p.m.	[NaCN] M	pH value	Potential V	Rate $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$
0,05	0,01	9,0	-0,926	1,33
0,05	0,01	10,0	-0,912	1,32
0,05	0,01	11,0	-1,076	1,29
5,0	0,01	8,9	-1,014	110
5,0	0,01	10,0	-1,100	101
5,0	0,01	11,9	-1,137	84
0,05	0,001	10,5	-0,836	1,03
0,05	0,002	10,5	-0,836	1,34
0,05	0,005	10,5	-1,098	1,32
5,0	0,001	10,5	-1,065	41,3
5,0	0,005	10,6	-1,102	99,7
5,0	0,010	10,5	-1,106	107

TABLE II

THE EFFECTS OF VARIOUS SULPHUR ANIONS

[Au] p.p.m.	[S] p.p.m.	Potential V	Rate $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$
0,05	0	-1,076	1,29
0,05	10(S <sup>2-</sup> )	-0,791	0
2,0	0	-1,138	48,9
2,0	10(S <sup>2-</sup> )	-1,050	31,4
2,0	10(SO <sub>3</sub> <sup>2-</sup> )	-1,122	57,7
5,0	0	-1,106	107
5,0	5(S <sup>2-</sup> )	-0,755	0
5,0	10(S <sup>2-</sup> )	-0,865	18,1
5,0	50(S <sup>2-</sup> )	-0,977	54,4
5,0	5(S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> )	-1,056	133
5,0	50(S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> )	-1,042	137
5,0	50(SCN <sup>-</sup> )	-1,073	123

which shows that, of the ions tested, only sulphide ion has a detrimental effect, particularly at the lowest concentration of gold. This inhibition is accompanied by a relatively large anodic shift in the potential during cementation, which is due to the passivating effects of sulphide on the anodic dissolution of the zinc (Fig. 5). The small but consistently higher rates obtained in the presence of thiosulphate or sulphite cannot at this stage be explained, and the effect warrants more extensive study.

The influence of various metals in solution on the rate of cementation is summarized in Table III. An important aspect of these results is the observation that relatively small amounts of lead can have a considerable inhibiting effect on the rate of cementation at low concentrations of gold. It should be pointed out that the results obtained in the presence of lead were often impossible to reproduce at gold concentrations of 2 p.p.m. and lower. This could possibly be associated with the hysteresis observed during the deposition of gold in the presence of lead as described earlier. An interesting observation was that no cementation at all occurred on a pure zinc surface from a solution containing 5 p.p.m. of gold and 0,005 M sodium cyanide at a pH value of 11,0. An increase in the pH value to 12, or the addition of 0,02 M sodium chloride or trace amounts of lead, initiated cementation that occurred at the mass-transport controlled rate. It is suggested that the impurity level of the lead in the sodium chloride is sufficient to account for the above observation in terms of which the cementation of lead produces a surface on which the high overpotential for gold deposition on zinc is reduced to an extent that

permits cementation. A more detailed study of the effect of the nature of the substrate on the deposition of gold is necessary.

Of the other metal ions tested, copper, nickel, and cobalt had no effect, whereas antimony and arsenic reduced the rate of cementation by about 20 per cent at the level of 1 p.p.m.. No explanation is at present available for these observations.

### Practical Implications

In this investigation, an attempt was made to apply modern electrochemical techniques to a detailed study of the half-reactions involved in the precipitation of gold. It is premature, without a detailed study of plant conditions and the nature of plant solutions, to advance unequivocal explanations of the various phenomena associated with such a complex chemical process; however, several possible implications regarding plant practice in terms of the mechanism can be discussed.

- (i) Under ideal conditions, the rate of reduction of aurocyanide ion by metallic zinc is controlled by diffusion of the aurocyanide to the zinc surface. This has been confirmed by laboratory-scale cementation experiments and mixed-potential measurements. The aim of a plant operation is to ensure that mass transport controls the process at all times, and any failures can therefore be attributed only to mechanical defects. The observation (Fig. 10) that the deposition of silver occurs at more anodic potentials than gold implies that the precipitation of silver can be expected to be less sensitive to operating conditions than that of gold, and it is suggested that a comparison of the silver and gold concentrations in cementation tailings could provide useful information on the possible source of inefficiency.
- (ii) That precipitation practice is not without frequent problems is apparent if the curves for each half-reaction are compared under similar conditions, as shown in Fig. 6. It should be apparent that the mixed potential in the absence of lead can be expected to be around -1,1 V, which is less than 0,2 V more cathodic than the potential at which the deposition of gold becomes diffusion controlled. This potential will, of course, become even more negative with decreasing gold concentration (approximately 0,06 V per decade), with the result that, in the absence of lead, diffusion-controlled deposition at a gold concentration of  $5 \times 10^{-8}$  M (0,01 p.p.m.) can be expected to occur only at potentials below about -1,2 V. A comparison of this value with those in Tables I to III shows that this value is never quite achieved during cementation. However, as shown in Fig. 6, the addition of even trace amounts of lead results in a 0,2 V positive shift in the cathodic curve, which then falls into a region where diffusion-controlled precipitation is possible at potentials in the range -1,0 V to -1,15 V. These observations demonstrate the nature of the crucial role that lead plays in the process. A further role for lead is the removal of sulphide ion as lead sulphide. In view of the ex-

TABLE III  
THE EFFECTS OF VARIOUS METAL IONS

[Au] p.p.m.	Metal present	[Metal] p.p.m.	Potential V	Rate $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$
0,02	Nil	0	-1,072	0,62
0,02	Pb	10	-1,043	0,10
0,02	Cu	10	-1,066	0,78
0,05	Nil	0	-1,108	1,33
0,05	Pb	1	-1,010	0,44
0,55	Pb	10	-1,056	0,32
2,0	Nil	0	-1,138	48,9
2,0	Pb	10	-1,066	18,8
4,0	Nil	0	-1,094	91,9
4,0	Ni	5	-1,090	108
4,0	Co	5	-1,098	88,9
4,0	Sb	1	-1,111	78,7
4,0	As	1	-1,098	83,6
5,0	Nil	0	-1,106	107
5,0	Pb	5	-1,045	133
5,0	Cu	5	-1,031	98
5,0	Cu	50	-0,952	101

tremely poisonous effect of this sulphide, this aspect cannot be overlooked.

- (iii) The addition of excessive amounts of lead can, as shown in Table III, inhibit cementation. This is probably due to a combination of the effects on both the dissolution of the zinc (Fig. 5) and the difficulty of nucleating gold on a lead surface (Fig. 9). Control of both the amount of lead added and its point of addition is therefore necessary to prevent such inhibition.
- (iv) The often-advocated plant technique of adding cyanide when in trouble has a fundamental basis only if excessive amounts of other oxidants are present in the solutions. Reference to Fig. 1(b) shows that the sum of all the cathodic processes, which include the precipitation of gold and other metals, and the reduction of other oxidants such as oxygen and ferricyanide, must be compensated for by an equivalent zinc-dissolution current. The latter is controlled by both the free cyanide concentration and the pH value (Figs. 3 and 4). If both

are low, passivation of the zinc (Fig. 2) is possible with a consequent anodic shift in potential and, therefore, cessation of gold deposition. In the absence of passivation, changes in the cyanide level will not be expected to affect the rate of precipitation significantly since, as demonstrated in Figs. 3 and 7, the influence of cyanide on the half-reactions tends to be compensatory. It should be pointed out that the same is not true of pH, in terms of which (Figs. 4 and 8) an increase can be expected to be beneficial. Although there could be other mitigating factors, it is suggested that more attention should be given to the control of pH as opposed to the expensive use of excessive amounts of cyanide. In this regard, the development of accurate techniques for the determination of free cyanide in the presence of large amounts of predominantly cyanide complexes with zinc and copper, must be given consideration before adequate control of the process can be implemented.

In conclusion, it should be pointed out that various other aspects of the precipitation process have been studied in some detail. These include the effects of various parameters such as the oxygen concentration and the presence of gold and lead on the corrosion of zinc and the kinetics of the cementation of lead by zinc. The results of these studies will be reported on in detail in future publications.

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