

Determination of leaching rates of precious metals by electrochemical techniques

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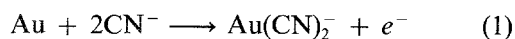
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The leaching rates of gold, silver, palladium and platinum in cyanide solutions have been determined from the corrosion potential and voltammograms of the anodic oxidation reaction. The order of reactivity was $\text{Au} > \text{Ag} > \text{Pd} > \text{Pt}$ and the leaching rate was a maximum at about pH 10 for each metal. An assessment was made of the applicability of PAR M342C Softcorr Corrosion Software, devised for computing corrosion currents, to the measurement of leaching rates of precious metals. The software does not yield accurate rates due to the nature of the individual oxygen reduction and metal dissolution processes, but could be applied to rapidly estimate the influence of variation in solution composition on the leaching of an individual metal.

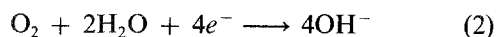
1. Introduction

The electrochemical nature of the leaching of metallic minerals is well established. The dissolution of precious metals in cyanide solutions was discussed in terms of electrochemical concepts before the end of the 19th century [1], and this subject was reviewed by Christy [2] in 1900 in a paper entitled 'Electromotive force of metals in cyanide solutions'.

In 1954, Kudryk and Kellogg [3] analysed the dissolution of gold in cyanide solution from a mixed-potential viewpoint and demonstrated that the leaching potential was predicted by the intersection of the current-potential curves for gold dissolution,



and oxygen reduction,



These authors concluded that "the dissolution rate and dissolution potential may be predicted within about 10% from the intersection of the anodic and cathodic current-potential curves". Cathro and Koch [4] subsequently confirmed that leaching rates calculated from electrochemical measurements agreed closely with values determined by solution analysis. Thus the electrochemical approach allows direct measurement of leaching rates and presents the opportunity to rapidly survey the influence on these rates of changes in solution composition. Other electrochemical studies of the leaching of gold [5-10] have focussed on understanding the detailed mechanism of the anodic and cathodic processes, and the concept of utilizing electrochemical techniques for the direct determination of leaching rates has not been pursued.

In the related field of metallic corrosion, the application of electrochemical techniques for the measurement of corrosion rates was first made in 1938 by

Wagner and Traud [11] in their classical paper in which mixed potential theory was conceived. The electrochemical approach for characterizing corrosion has been developed considerably since that time [12] and has been promoted in the 1970s and 1980s through the improvement of instrumentation and procedures, particularly with regard to computer-controlled operation.

In this publication, electrochemical studies are presented on the dissolution of gold, silver, palladium and platinum in cyanide media and an assessment is made of the applicability of computer-based techniques devised for determining corrosion rates to the determination of leaching rates.

2. Experimental details

A PARC model 273 potentiostat/galvanostat was used for the electrochemical measurements. The instrument was interfaced through a National Instruments PC2A GPIB controller to an IBM-PC/XT compatible personal computer running the PARC model M342C Softcorr Corrosion Software. This software enabled ready control of the potentiostat for making electrochemical measurements in the vicinity of the corrosion potential. The raw data were stored on disc at the end of the measurements and were available for subsequent plotting and evaluation by the M342C and other applications software.

The PARC 273 potentiostat employs a differential input electrometer which, although having a high input impedance, $> 10^{10} \Omega$, is apparently unable to tolerate an imbalance in the input arms of $> 20 \text{ k}\Omega$ [13]. Values of this order and above can be established with glass-sleeve junctions and small Luggin capillaries, particularly when low conductivity solutions are being used. To overcome instability problems associated with this characteristic, a fine platinum wire was positioned within the reference compartment Luggin

to reduce ohmic resistance, and a sintered plug type reference electrode employed.

All solutions were prepared from general purpose grade (minimum assay 97%) NaCN. All other reagents were analytical grade. Doubly distilled water which was subsequently deionized through a Milli-Q System (Millipore Corporation, Mass.) was used at all times.

Measurements were carried out with a conventional 3-compartment cell maintained at 25°C in a water bath. Potentials were recorded with respect to a standard calomel electrode (SCE). Pure noble metals (supplied by Engelhard Industries: Au and Pt, and P.S.P Industries Pty Ltd., Thomastown: Ag and Pd) were used for the working electrodes which were constructed from 3 mm diameter rods of the four metals under study by attaching them to brass holders with silver epoxy and encapsulating in Araldite D (Ciba-Geigy). The holder was threaded to enable the electrode to be attached to a Beckman 'rotating electrode' controller. The active end of each electrode unit was machined to expose a disc of the metal which was then polished with 5 µm alumina paste. Electrodes were cleaned ultrasonically after each polishing process. Before each electrochemical run, they were first polished, then etched at room temperature in 1 mol dm⁻³ NaCN to produce an active surface [14]. A minimum etching period for each metal was necessary to establish a reproducible corrosion potential. Silver required a period of 15 min to reach a stable potential, whereas gold needed about twice that time. Palladium did not appear to require any pretreatment period; the results for this metal were the most reproducible of the four metals investigated. The corrosion currents for platinum were low and it was difficult to evaluate the effect of pretreatment time on dissolution rate. However, to ensure reproducibility of the method, all electrodes were given a 30 min etching. After etching, the electrodes were rinsed briefly with distilled water and then immersed, still wet, into the cell solution.

Determinations using the PARC M342C software were made in air-saturated solutions with the electrode rotated at a convenient speed of 4 s⁻¹, except where otherwise stated. When the potential reached a constant value, usually within 2 min. data were collected on the first scan by the 'TAFEL' function of the software which sweeps anodically 250 mV each side of the corrosion potential. The corrosion information was then calculated using the 'PARCalc' routines. The actual dissolution rates were then determined by de-oxygenating the solution with high-purity nitrogen for 30 min. and then running an anodic sweeping voltammogram across the region of the corrosion potential previously determined under the air-saturated conditions. The use of the initial scans for these determinations ensured that the surface of the electrode suffered minimum change from the oxidation reactions occurring. Scan rates of 2 mV s⁻¹ were selected for these measurements being slow enough to allow virtual equilibration of the system without the inconvenience of long measuring times. The current on the voltammogram at this corrosion potential was taken

as the dissolution current. Most determinations were made in 0.1 wt % (0.02 mol dm⁻³ or 0.02 M) sodium cyanide solutions of pH 8–12. The solutions were buffered using various combinations of NaHCO₃ and Na₂CO₃ concentrations while maintaining a constant total concentration of 0.1 M.

The characteristics of oxygen reduction on gold were determined in a pH 10 solution in which the sodium cyanide was replaced by sodium chloride, and added at the usual cyanide concentration of 0.02 M. This addition of sodium chloride ensured that the ionic strength of the medium was approximately the same as that for the solutions containing cyanide.

The surface roughness of the platinum, palladium and gold electrodes was measured in 1 M H₂SO₄ from the adsorption of hydrogen on platinum and oxygen on the other two metals [15]. The surface roughness of silver is not amenable to either method of determination.

3. Results and discussion

3.1. Eh-pH diagrams

Figure 1 presents Eh-pH diagrams for (a) gold, (b) silver, (c) palladium and (d) platinum in 0.02 M cyanide solutions at 25°C prepared employing the CSIRO Thermochemistry System [16]. The diagrams reveal a wide stability region for the complex cyanide ions of each metal, viz., Au(CN)₂⁻, Ag(CN)₂⁻, Pd(CN)₄²⁻ and Pt(CN)₄²⁻. A gold(III) complex, Au(CN)₄⁻, occupies a stability domain above that of the gold(I) complex (Fig. 1a); this species will not play a significant role in gold leaching under the present solution conditions since the potential region is more positive than the oxygen line.

The metal/metal cyanide boundaries are independent of pH above 9.2, but, below this value they are pH dependent due to the stable cyanide species in solution becoming HCN. For each metal, the complex cyanide ion domain exists below the oxygen line and hence, from the thermodynamic viewpoint, leaching of all four metals is possible in cyanide solutions containing oxygen. The difference in the potentials of metal cyanide ion formation and oxygen reduction reflects the free energy difference driving the leaching reaction. It can be seen that this follows the order Au > Ag > Pd > Pt.

3.2. Voltammetry

Linear potential sweep voltammograms in 0.02 M cyanide at pH 11.2 for (a) gold, (b) silver, (c) palladium and (d) platinum over the same potential range are presented in Fig. 2. The vertical lines marked on the figure are the reversible potentials for the metal/metal cyanide ion couples obtained from Fig. 1.

The voltammogram for gold (curve a) is similar to that presented by previous workers [5, 7, 9, 10] who identified the various features in terms of a mechanism involving adsorbed cyanide and hydroxide species.

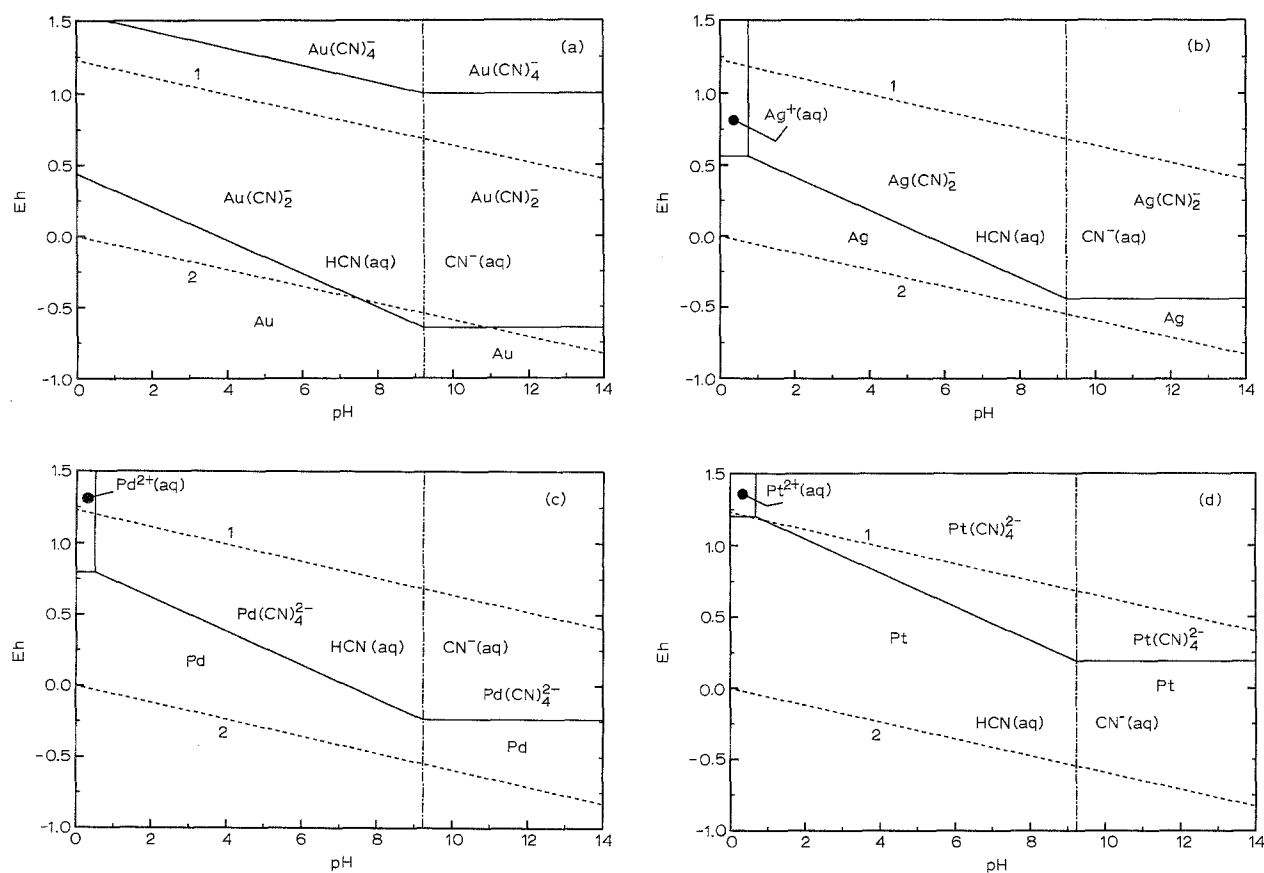


Fig. 1. Eh-pH diagrams for (a) gold, (b) silver, (c) palladium and (d) platinum in 0.02 M NaCN at 25°C. Diagrams are calculated for unit activity of metal and ionic activity of 0.0001. H₂O stability limits: 1 = oxygen, 2 = hydrogen (both at unit activity).

However, the appearance of a diffusion limited region between -100 mV and 300 mV rather than peaks, most probably results from the lower pH values and cyanide concentration adopted, although some curves presented in [5] do show a tendency for diffusion control in this region. The decreased current density of the adsorption peak at -600 mV, reflects the lower cyanide concentration used by the present workers. The thermodynamically predicted oxidation potentials are not necessarily observed under the dynamic conditions found during voltammetry, particularly where kinetics are slow. In the case of gold, the slow step is generally considered to be the adsorption of the cyanide anion onto the electrode surface; this probably accounts for the displacement of the reversible potential from the thermodynamic value. The passivation of the gold surface at positive potentials is explained by oxygen adsorption which is known to take place in the relevant potential region for gold dissolution [15].

Silver gives rise to an uncomplicated voltammogram (curve b) in which the anodic current increases rapidly from the reversible potential to a limiting current. The latter is mass transport controlled since the current was found to be proportional to $\omega^{1/2}$, where ω is the electrode rotation speed [17]. The limiting process will be transport of cyanide ions to the electrode surface. It is clear that the current in the middle potential region on gold (curve a) is also mass transport controlled since it has the same value.

It can be seen from Fig. 2 that the dissolution

current reaches significant values at potentials much closer to the reversible value for silver than for gold. Thus, the thermodynamic advantage of gold is offset by the more rapid kinetics of the silver dissolution process.

The voltammogram for palladium (curve c) displays an anodic peak at -0.65 V which corresponds to desorption of the hydrogen that was adsorbed in the lower potential region of the scan. This anodic peak is followed by an increase in current commencing close to the reversible potential for the dissolution of palladium to form $\text{Pd}(\text{CN})_4^{2-}$. The inhibition of the dissolution process commencing at ~ 0.4 V could be due to oxygen adsorption which occurs at about this potential in alkaline solution [18].

Platinum gives rise to a voltammogram (curve d) that exhibits no obvious features which can be identified with metal dissolution. This indicates that the rate of dissolution of platinum is significantly less than those of the other metals investigated. It should be noted that the reversible potential for platinum dissolution is in the region in which oxygen is adsorbed [18]. This could explain the low activity of platinum for dissolution in cyanide since adsorbed oxygen passivates both gold and palladium.

3.3. Leaching rates

It was pointed out in the Introduction that the leaching of precious metals proceeds via the simultaneous

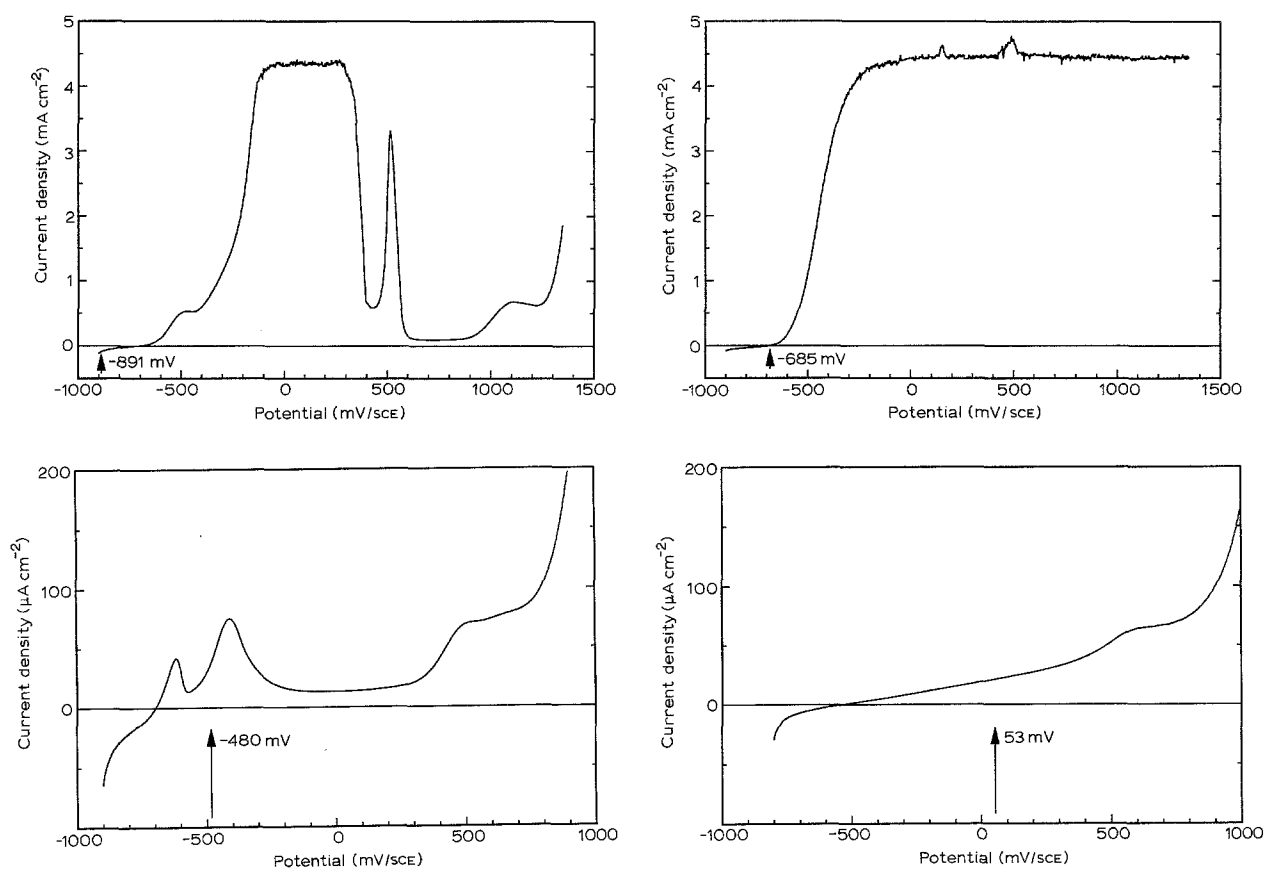


Fig. 2. Linear potential sweep voltammograms in 0.02 M NaCN; pH 11.2; temp. 25°C; sweep rate 2 mV s⁻¹; rotation rate 4 s⁻¹; for (a) gold, (b) silver, (c) palladium, and (d) platinum.

anodic dissolution of the metal and cathodic reduction of oxygen. Thus, the leaching rate is equal to that of the anodic reaction at the leaching (i.e. corrosion) potential. This is illustrated by the data presented in Fig. 3 for the behaviour of the gold electrode in 0.02 M cyanide at pH 10. Curve (a) is the output of the electrochemical system for an excursion across the potential region of the reversible value for Au/Au(CN)₂⁻ couple in de-aerated solution. The anodic segment represents gold dissolution, while the cathodic process is probably hydrogen evolution. Curve (c) is that obtained for oxygen reduction in an air-saturated,

cyanide-free solution at pH 10. The oxygen reduction current is essentially potential independent, as it is mass-transport controlled under these conditions.

The potential at which the gold dissolution current (a) and oxygen reduction current (c) are equal in magnitude should correspond to the corrosion potential for gold dissolution in air-saturated solution. Curve (b) in Fig. 3 is the output obtained from a potential excursion in air-saturated solution and it can be seen that the corrosion potential observed is indeed, the same as that predicted from the algebraic sum of the two other curves. The currents recorded in the aerated cyanide solution should be the sum of the currents contributed by the oxygen reduction and gold dissolution processes occurring at that potential. It can be seen that this is the case within experimental error.

The dissolution current for gold under the conditions of Fig. 3 should be mass-transport controlled since the oxygen current that determines the dissolution current is mass-transport controlled. This was found to be the case; the dissolution current varied linearly with $\omega^{1/2}$.

The above results confirm that the dissolution current can be determined by measuring the anodic current in deaerated solution at the potential corresponding to the corrosion potential in aerated solution. Using this approach, the dissolution currents for the four metals have been determined as a function of solution pH in 0.02 M cyanide. The dissolution rate in

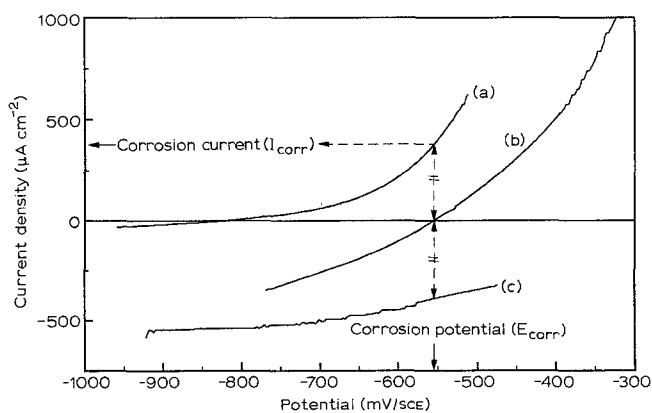


Fig. 3. Composite voltammograms showing coincidence of potentials for equal magnitude of oxygen reduction current (curve C) and gold dissolution current in de-aerated solution (curve A), with the corrosion potential of gold in aerated solution (curve B). Temp. 25°C; sweep rate 5 mV s⁻¹; rotation rate 4 s⁻¹.

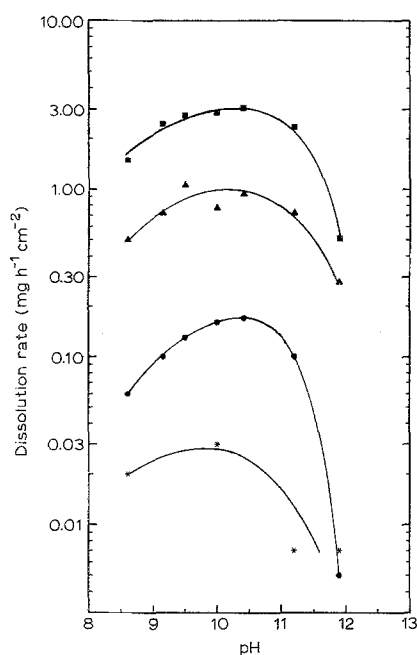


Fig. 4. Effect of pH on dissolution rate for the noble metals in 0.02 M NaCN at 25°C. (■) gold, (▲) silver, (●) palladium, (*) platinum.

terms of weight dissolving was readily derived from the dissolution current since:

$$r = (M/nF)i_{\text{diss}} \quad (3)$$

where r is the dissolution rate per cm^2 of metal surface, M is the atomic weight of the metal, and n is the number of electrons in the anodic dissolution reaction. The results are presented in Fig. 4 in terms of the dissolution rate (in $\text{mg h}^{-1} \text{cm}^{-2}$) calculated from the dissolution current, taking the dissolution of gold and silver to be a 1-electron and that of palladium and platinum to be a 2-electron process (Fig. 1). It can be seen from Fig. 4 that, for each metal, the rate is a maximum in the region of pH 10. The decline in activity on the acidic side reflects the decrease in concentration of the cyanide ion as the pH drops below the pK_a for HCN at pH 9.2. At high pH values, the fall in dissolution rate is probably due to the fact that the driving force for the process, the difference in potential of the metal dissolution and oxygen reduction reactions, decreases with increase in pH (see Fig. 1).

The corrosion potentials found for gold and silver under identical conditions were close to the same values (*ca.* -550 mV at pH 10). Since the dissolution rates for silver were found to be less than those for gold (Fig. 4), the oxygen reduction activity for the former metal must be lower than that of the latter under the experimental conditions investigated.

The surface roughness of the gold, palladium and platinum electrodes following determination of the dissolution rates was found to be 15, 3 and 4, respectively. The severely roughened nature of the gold electrode was also evident from optical microscopic examination of the surface. It is apparent that one aspect of the activation, pretreatment process used in these studies is to increase the real surface area of the

metal. The extent of roughening differs for the different metals investigated. Thus, the dissolution rates in Fig. 4, although calculated on the basis of geometric surface area, do not relate to the same unit real area of electrode surface. However, they are comparative values under identical leaching conditions since the pretreatment was etching in a cyanide leachant solution. The relative rates in Fig. 4 are as expected from general knowledge of conventional leaching processes.

3.4. Corrosion rates from the M342C program

The M342C software statistically fits the experimental data to the Stern–Geary model for a corroding system [19]. The PARCalc routine automatically selects the data that lie within $\pm 200 \text{ mV}$ of the corrosion potential. It deletes information in any passivation region from the calculations and iteratively arrives at a best fit of the data to yield values for the Tafel slopes from which the corrosion current is calculated. The output includes an assessment of the precision of the computed value. The corrosion current can also be derived from polarization resistance [19] calculations. This program involves a linear regression analysis of corrosion data acquired within 10 mV (default; other ranges are user selectable) of the corrosion potential, applying the Tafel constants determined by the PARCalc routine.

Figure 5 presents the corrosion currents for silver obtained from the M342C PARCalc and polarization resistance programs compared with those determined directly from the anodic current in de-aerated solution at the corrosion potential. It can be seen that the currents derived from the two computer methods are approximately equal but differ significantly from the correct values.

It was also found that the direction of the error in the computed data depended on the system, such that the results for gold were about one half the correct values whereas those for silver were double. Thus the results calculated from the programs suggest that silver leaches faster than gold which is the opposite to the values determined directly and to those found in

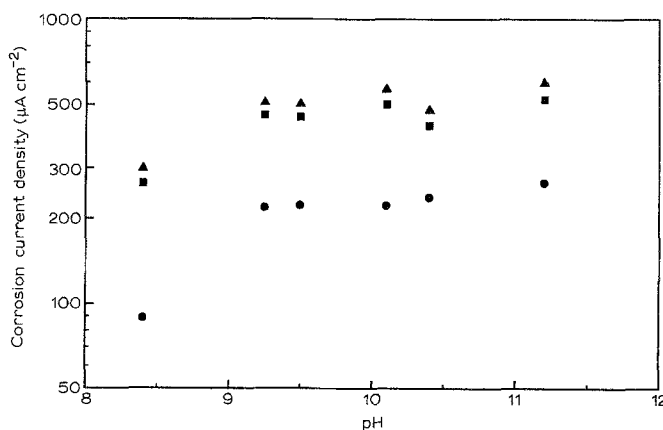


Fig. 5. Comparison of corrosion currents for silver determined by PARCalc Tafel software (■), polarization current software (▲), and the voltammetric method (●), in 0.02 M NaCN at 25°C.

other leaching studies. These errors most likely derive from the lack of significant Tafel regions for both cathodic and anodic processes. The former has a significant mass transport component and the latter displays passivity at potentials sufficiently removed from the corrosion potential for the cathodic current component to be insignificant. Indeed, the M342C program indicated that the fit of the data to the Stern-Geary equations was poor. Nevertheless, Fig. 5 shows that the computed values do follow the changes in rate associated with change in pH, and thus the programs could be used to rapidly survey the influence of additives and other changes in solution composition on the leaching rate of a particular precious metal.

4. Conclusions

1. Leaching rates of precious metals in cyanide solutions can be determined from measurement of the corrosion potential and voltammograms of the anodic dissolution process.

2. The order of activity is Au > Ag > Pd > Pt.

3. The leaching rate for each metal is a maximum at a pH of about 10.

4. Leaching rates derived from the PAR M342C Softcorr Corrosion Software can be in error by a factor of two. However, the software could be used to rapidly survey the influence of solution composition on the leaching of a particular precious metal.

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References

- [1] E. B. Wilson, *Trans AIME* **27** (1897) 821-46.
- [2] S. B. Christy, *ibid.* **30** (1900) 864-946.
- [3] V. Kudryk and H. H. Kellogg, *J. Metals* **6** (1954) 541-48.
- [4] K. J. Cathro and D. F. A. Koch, *Proc. Aust. IMM* **210** (1964) 111.
- [5] K. J. Cathro, *ibid.* **207** (1963) 391.
- [6] K. J. Cathro and D. F. A. Koch, *J. Electrochem. Soc.* **111** (1964) 1416.
- [7] T. P. Pan and C. C. Wan, *J. Appl. Electrochem.* **9** (1979) 653.
- [8] M. E. Wadsworth, *Mining Engineering* **37** (1985) 557.
- [9] D. W. Kirk, F. R. Foulkes and W. F. Graydon, *J. Electrochem. Soc.* **125** (1978) 1436.
- [10] M. J. Nicol, *Gold Bulletin* **13** (1980) 105.
- [11] C. W. Wagner and W. Traud, *Z. Elektrochem.* **44** (1938) 391.
- [12] F. Mansfeld, in 'Advances in Corrosion Science and Technology', Vol. 6 (edited by M. G. Fontana and R. W. Staehle), Plenum, New York (1976) pp. 163-262.
- [13] R. Rogers, EG&G Princeton Applied Research Corp., private communication.
- [14] K. J. Cathro, CSIRO Division of Mineral Products, private communication.
- [15] R. Woods, in 'Electroanalytical Chemistry', Vol. 9 (edited by A. J. Bard) Marcel Dekker, New York (1976) pp. 1-162.
- [16] A. G. Turnbull and M. W. Wadsley, CSIRO Thermochemistry System, Version 5.1. CSIRO, Division of Mineral Products, Port Melbourne.
- [17] V. G. Levich, 'Physicochemical Hydrodynamics', Prentice-Hall Inc. New Jersey (1973).
- [18] M. R. Tarasevich, V. S. Vilinskaya, and R. Kh. Burshtein, *Elektrokhim.* **7** (1971) 1200.
- [19] M. Stern and A. I. Geary, *J. Electrochem. Soc.* **104** (1957) 56.