The kinetics of the dissolution of colloidal silver in cyanide medium and application to the control of the cyanidation process

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Synopsis

The kinetics of the dissolution of colloidal silver in aerated cyanide solutions has been investigated with the aim of developing a relatively rapid and convenient method for monitoring the 'leaching power' of solutions typically used in the cyanidation process. Experimental results obtained are consistent with an electrochemical model, in which the mixed potential is set up in the active region of the polarization curve for the anodic dissolution of silver, giving rise to a rate of dissolution which is controlled by the rate of mass transport of either cyanide or oxygen to the surface of the silver. The rate of dissolution of colloidal silver was found to respond to variations in the reactant concentrations in a similar manner to gold (and silver) in a typical free-milling ore. The use of this technique for the monitoring and control of the cyanide leach process is discussed.

Introduction

The cyanidation process has been used as the principal means for the extraction of gold from its ores for over a century. However, satisfactory control of the dissolution process by adjustment of the cyanide and/or dissolved oxygen concentrations to their optimum values consistent with efficient extraction and minimal cost has not yet found wide-spread acceptance.

While there is instrumentation which is used to monitor the concentrations of free cyanide and dissolved oxygen under plant conditions, integration of the results of such measurements into suitable control and optimization strategies has not developed to any noticeable extent.

An alternative approach involves some means of directly or indirectly measuring the rate of dissolution of gold in the leach solution or pulp. Although potentially useful, mixed potential measurements of gold or silver electrodes have been shown to suffer long-term variations and interference from impurities such as sulphide ions in typical leach solutions.

A previous study[1] has shown that the rate of dissolution of colloidal gold particles in aerated cyanide solutions is relatively rapid with half-lives of the order of minutes. The results showed, however, that the rate of dissolution of the colloid does not respond in the same way to variations in the concentrations of cyanide and oxygen as does a gold particle in a typical ore. This was interpreted in terms of a mechanism in which colloidal gold dissolves in the passive state. The use of colloidal gold is therefore of limited value in this respect and it was felt that silver, which does not passivate over the short term in alkaline cyanide solutions, could be a suitable alternative. Aside from the above work on the dissolution of colloidal gold, it appears that the only work on the rates of dissolution of colloidal metals is that of Miller and Herz[2] who carried out semi-quantitative experiments on the dissolution of colloidal silver in aqueous solutions containing various ligands known to complex silver ions. Pal *et al*[3] used colloidal silver in a spectrophotometric and conducto-metric titration of cyanide but did not determine the rates of dissolution.

The usefulness of a silver colloid in some kind of cyanidation process control device derives from the fact that its colour (absorption maximum around 420nm), which can easily be measured, varies in a predictable way as the colloid dissolves, and the fact that the colloid should react much more rapidly than bulk metal, since the specific surface area in the colloidal phase is so much greater (some $100m^2$ per gram of silver in a colloid of particle diameter 6nm). Depending on the rate of dissolution of the colloid, this offers the potential for a relatively rapid response in any process control device.

The present investigation is aimed at assessing the rate of dissolution of colloidal silver particles as a function of the concentrations of cyanide and oxygen as a precursor to the development of cyanidation process control devices using the colloid.

The kinetics of the dissolution of colloidal silver in cyanide medium

Experimental

Stabilized colloidal silver was prepared according to the method of Pal et al[3] in which a dilute solution of silver nitrate is reduced with ascorbic acid at pH 8 in the presence of gelatine which acts to stabilize the colloid against coagulation and precipitation. The pH of the colloidal suspension was increased to 10 by the addition of sodium hydroxide prior to use in the kinetic runs. Previous workers[2] have shown that colloids prepared by this method have mean particle sizes in the range 6 to 12nm. Measurement of the absorbance at 420nm of the yellow colloid solutions of varying concentrations using a Varian Model 635LC spectrophotometer with 1 cm cuvettes confirmed that Beer's law was obeyed at the silver concentrations of 4.10^{-6} to 4.10^{-5} mol/l (0,4 to 4 ppm) used in this study.

Kinetic runs for the dissolution were obtained by recording the absorbance at 420nm as a function of time. 3ml of a colloid suspension was placed in a thermostatted cuvette in the spectrophotometer, and 1ml of sodium cyanide solution was rapidly injected into this volume. The chart recorded the decrease in the absorbance with time as the cyanide reacted with the colloid. The colloid was diluted to the point where the amount of dissolved oxygen in the solution (8 ppm) was at least 10 times in excess of the stoichiometric amount required to dissolve all of the silver in the colloid which was generally 2.10^{-5} mol/l (2 ppm). For most runs, a large excess of cyanide was also added to the colloid. These conditions allow the concentrations of the two reactants, viz. oxygen and cyanide, to be assumed constant over the course of the batch dissolution run.

The behaviour of the dissolution of the stabilized colloid with respect to changing reactant concentrations was investigated. The cyanide concentration was varied by adding increasingly concentrated cyanide solutions to the colloid while the oxygen concentration was varied by saturating both of the solutions with air or with oxygen by bubbling oxygen through the solutions for at least 10 minutes before mixing to start the reaction.

Unless stated otherwise, all solutions were air-saturated and all experiments were conducted at a constant temperature of 24 ± 1°C.

Results

In the previous study[1] of the dissolution of colloidal gold, the fractional dissolution of gold at any time was found to be equal to the fractional change in absorbance of the colloid as a result of reaction. This result was surprising given that, as the colloidal particles shrink, their absorbance peak should shift to lower wavelengths but remain of similar height[2]. The colloidal gold appeared to be behaving in a way identical to a dissolved species in solution. A similar observation was made by Pal et al[3] in the development of an analytical method for cyanide using stabilized silver colloids and it has been assumed that the same behaviour applies in the case of this study.

The absorbance of the colloidal suspension was found to decay smoothly to approximately zero with a half-life of the order of minutes. It was found that plots of the logarithm of the absorbance versus time were linear and the slopes of such plots were used to derive pseudo-first-order rate constants.

Table I

Effect of oxygen concentration on the rate of dissolution

[CN⁻] mol/l	Rate constant, min⁻¹	
	Air	Oxygen
$2,4.10^{-4}$	0,18	0,23
$4,0.10^{-3}$	0,34	0,48
$1,0.10^{-2}$	0,31	>1,3

Table II

Effect of temperature and lead ions on the rate of dissolution (0,01 mol/l cyanide, aerated solutions)

Temp. °C	Rate constant, min⁻¹
24	0,31
30	0,56
40	1,00
50	1,60
65	2,38
24*	0,32

*1.10^{-5} mol/l lead ions present

Thus, Figure 1 depicts the variation in the reaction rate constants with increasing cyanide concentration in aerated solutions at pH 10 from which it is apparent that the rate increases with increasing cyanide concentration up to a concentration of about 0,004 mol/l (100 ppm) above which the rate is independent of the concentration.

Variation of the dissolved oxygen concentration at various cyanide concentrations gave results (Table I) which show that the rate is largely independent of the oxygen concentration at low cyanide concentrations. At concentrations of cyanide of 4.10^{-3} mol/l and above, the rate of dissolution increased with increasing oxygen concentration.

Variation of the temperature in the range 30°C to 65°C in aerated solutions containing 0,01 mol/l (260 ppm) of cyanide showed (Table II) that the rate increased with temperature and a value for the activation energy of 26 kJ/mol was derived after making a correction for the variation of the aqueous solubility of oxygen from air as a function of temperature.

Addition of lead ions as lead nitrate at a concentration of 1.10^{-5} mol/l (2 ppm) was found (Table II) to have no measurable effect on the rate of dissolution at cyanide concentrations of 2.10^{-4} mol/l (5 ppm) and 4.10^{-3} mol/l (100 ppm) cyanide.

Discussion

The dissolution of silver and gold in cyanide medium may be understood[4] in terms of a mixed potential electrochemical model. The anodic process involves the dissolution of the metals to give the complex ions $Ag(CN)_2^-$ and $Au(CN)_2^-$. In the case of silver, the anodic reaction has been shown[5] to be relatively simple with a smooth transition from activation-controlled dissolution at low overpotentials to potential-independent dissolution at high overpotentials where the rate is controlled by mass transport of cyanide ions to the metal surface. In the case of gold, much work has demonstrated[6]

The kinetics of the dissolution of colloidal silver in cyanide medium

that the anodic polarization curve in cyanide medium is complex and exhibits several active-passive transitions as a result of the potential and crystal plane specific formation of adsorbed layers of gold hydroxides and/or cyanide on the reacting gold surface. The cathodic process in the case of both metals entails the reduction of oxygen to produce either hydrogen peroxide or hydroxyl ions.

During dissolution, the potential of the metal relative to the solution establishes a mixed potential at which the current densities of the anodic and cathodic processes are equal, as depicted in Figure 2 for the dissolution of silver. It is apparent that, depending on the relative concentrations of cyanide and dissolved oxygen, the rate of dissolution can be controlled by mass transport of either reactant to the metal surface.

From Figure 1 it is clear that, as expected in terms of this model, the rate of dissolution increases with increasing cyanide concentration at low concentrations but becomes independent of the concentration above about 0,004 mol/l (100 ppm) in aerated solutions. Also shown in Figure 1 are data taken from a publication by Li *et al*[5] for the dissolution of a rotating silver disc in aerated cyanide solutions under similar conditions. The similar shapes of the two curves suggests that mechanism of the dissolution of the colloid is identical to that of bulk silver metal. The following additional observations also support this conclusion.

➤ The increasing dependence of the rate on the oxygen concentration as the cyanide concentration increases is consistent with the above model.

➤ The observed activation energy for the dissolution of 26 kJ/mol is indicative of mass transfer controlled process, which should have an activation energy in the range of 20-30 kJ/mol.

➤ The absence of an influence of lead ions (at the concentration tested) on the rate of dissolution of the colloid is also characteristic of the dissolution behaviour of silver which is not subject to the well-known[6] depassivating effect of lead ions on the dissolution of gold in cyanide solutions.

Although the above considerations suggest that the dissolution of the colloid is similar to that of bulk metal, it is interesting to compare the relative rates. Thus, calculation of the initial rate of dissolution of the colloid (assumed surface area $100 m^2/g$) from the maximum value shown in Figure 1 yields a specific rate of dissolution of 5.10^{-9} g cm^{-2} s^{-1}. This is some two orders of magnitude less than the rate of 5.10^{-7} g cm^{-2} s^{-1} found by Li *et al*[5] and shown in Figure 1.

This difference in the rates of dissolution can be attributed to the presence of an adsorbed layer of the macromolecule, gelatine, on the surface of the colloid. As found in the case of the dissolution of colloidal gold, mass-transport of cyanide and oxygen to the metal surface can be reduced by up to several orders of magnitude in the presence of adsorbed organic molecules which are added to stabilize the colloid against coagulation. In fact, without this retarding influence on the rate of dissolution of particles of colloidal dimensions, the rates would, as demonstrated[7] in the case of gold, be too rapid to experimentally measure by conventional

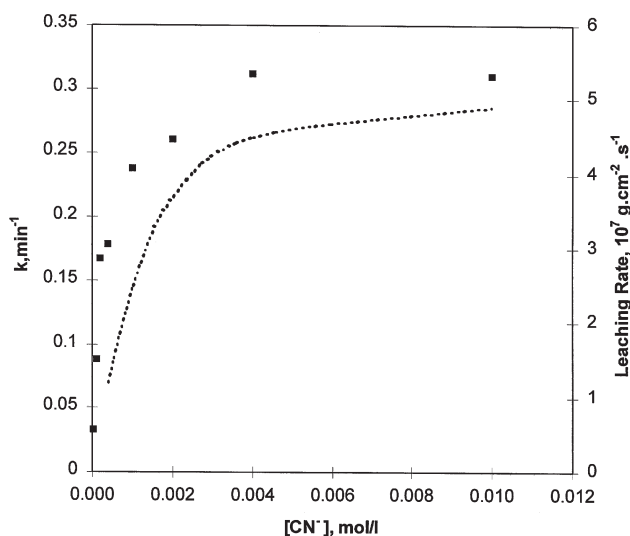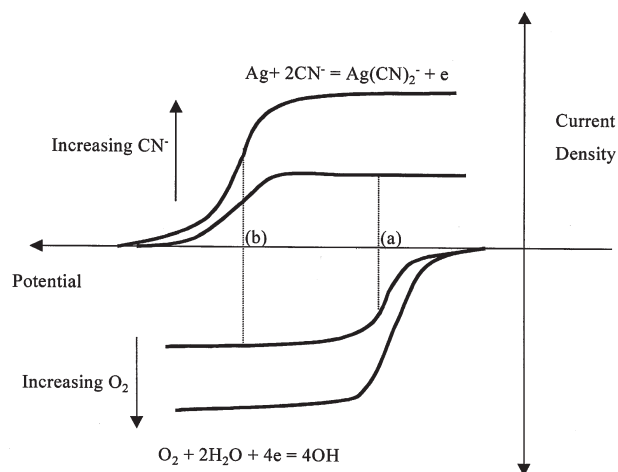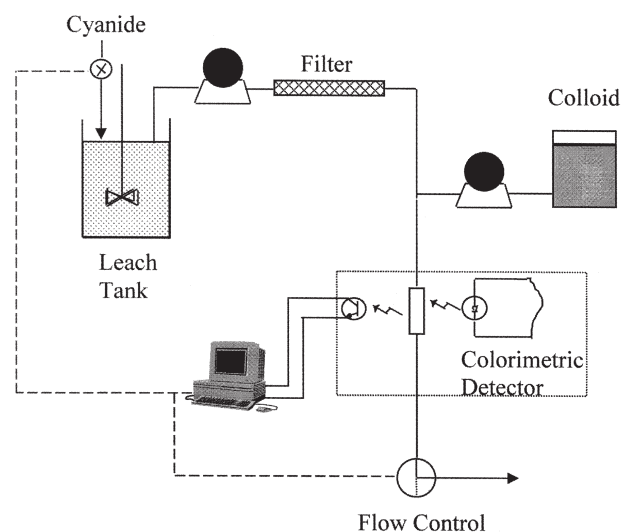Figure 2—Schematic current-potential curves for the dissolution of silver in aerated cyanide solutions

Figure 1—Variation of the first-order rate constant with the concentration of cyanide in aerated solutions (■). Also shown is data on the dissolution of silver metal from Li *et al*[5] (------).

Figure 3—Possible leach monitoring and control system using a colorimetric method for assessment of the rate of dissolution of colloidal silver

The kinetics of the dissolution of colloidal silver in cyanide medium

techniques. Miller and Herz[2] also found that the rate of dissolution of colloidal silver in aerated solutions of non-complexing acids was reduced by four orders of magnitude in the presence of 0,5% gelatine.

Application to process control and optimization

The dissolution of colloidal silver has been found to occur at a rate which is conveniently rapid with a half-life under typical cyanidation conditions of about 2 to 3 minutes. This will enable monitoring of the solution from various stages of the process to be carried out at intervals as frequently as every 5 minutes. The measurement technique is relatively simple, reliable and robust in that a suitable light-emitting diode/photodiode combination as a colorimeter will provide the necessary sensitivity and long-term stability in either a single or double-beam configuration. There are several possible methods of obtaining the necessary dissolution rate data, one of which is shown schematically in Figure 3. In this case, leach pulp from a selected point in the circuit is filtered, mixed with a small quantity of the colloidal silver suspension, and the absorbance monitored as a function of time for a period of several minutes. This is conveniently carried out in a simple flow system as shown. The absorbance data can be analysed on-line in order to derive, for example, an estimate of the half-life of the dissolution reaction. The problem of obtaining a suitable filtered solution from the leach pulp is similar to that which is required for current cyanide analysers and optical compensation for small amounts of very fine suspended solids in the sample is relatively easily accomplished by, for example, using a double-beam system.

It is apparent from Figure 1 that the optimum leach conditions will be achieved at the knee of the curve at which concentration of cyanide the rate will be maximum and that no improvement can be achieved by increasing the concentration beyond this point. The position of this optimum cyanide concentration will depend on the dissolved oxygen concentration. It is therefore possible to devise a relatively simple control and optimization strategy which will maximize the dissolution rate without incurring excessive cyanide consumption as a result of operating at cyanide concentrations which are higher than necessary for the prevailing dissolved oxygen level.

Conclusions

The dissolution characteristics of dilute colloidal silver dispersions in aerated cyanide solutions have been established. Results obtained from a number of experiments are consistent with a mechanism of the dissolution process which occurs as a typical mixed potential electrochemical process, the rate of which is controlled by mass transport of either cyanide ions or dissolved oxygen to the colloidal metal surface.

Thus, it has been shown that, unlike colloidal gold, the characteristics of the dissolution of colloidal silver in alkaline cyanide solutions are similar to those found for the leaching of bulk silver metal. The relative rate of dissolution of the colloid is lower than expected and this is probably due to the presence of gelatine adsorbed on the colloid surface.

The use of the rapid and conveniently measured reaction of silver colloids with aerated cyanide solutions provides a potentially useful method for the assessment of the relative 'leaching power' of a solution which could have application in the control and optimization of the cyanidation process.

References

1. NICOL, M.J., McCARTHY, A.J. and COLEMAN, R.G. The Mechanism of the Dissolution of Colloidal Gold in Cyanide Medium. Submitted to J. Electrochem. Soc. 1997.

2. MILLER, W.J. and HERZ, A.H. Characterization and Oxidation of Colloidal Silver. *Colloid and Interface Science, vol. IV. Hydrosols and Rheology*, M. Kerner, (ed.). Academic Press. 1976. pp. 315–329.

3. PAL, T., GANGULY, A. and MAITY, D.S. Determination of Cyanide Based on its Reaction with Colloidal Silver in the Presence of Oxygen. *Anal. Chem.*, vol. 58. 1986. pp. 1564–1566.

4. NICOL, M.J., FLEMING, C.A. and PAUL, R.L. *The Extractive Metallurgy of Gold*, G.G. Stanley, (ed.). Chap. 5. South African Institute of Mining and Metallurgy, Johannesburg . 1987.

5. LI, J., ZHONG, T. and WADSWORTH, M.E. Application of Mixed Potential Theory in Hydrometallurgy. *Hydrometallurgy*. vol. 29. 1992. pp. 47–60.

6. NICOL, M.J. The Anodic Behaviour of Gold. II. In Alkaline Solutions. *Gold Bulletin*. vol. 13. 1980. pp. 105–111. ◆