

Electrochemistry and Leaching Kinetics of Gold-Silver Alloys in Cyanide Solutions

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ABSTRACT

The dissolution behavior of gold and silver from gold-silver alloys in aerated cyanide solutions has been investigated by an electrochemical means as well as a direct measurement of gold and silver ions reported in the bulk solution as a function of time using rotating disc electrodes. The variables studied included oxygen partial pressure, rotating speed of the disc, concentration of cyanide, temperature and composition of the alloys. The dissolution potential and the rate of dissolution were obtained in view of the anodic and cathodic current-potential relationships. The results were discussed in terms of the mixed potential theory. The results showed that the dissolution rate of gold and silver from the alloys was controlled partially by chemical reaction, but largely by transport of either oxygen or cyanide, depending on their relative concentration under the experimental conditions employed in this study.

1. Introduction

Recycling of many metals has become very important. For example, in 1994 the united states refinery production of silver and gold was estimated at 4000 and 400 metric tons respectively, of which 50% and 37.5% respectively were reclaimed 400 metric tons respectively, of which 50% and 37.5% respectively were reclaimed from scrap.¹⁾

In order to achieve their high mechanical strength, good corrosion resistance, low cost, and sharp appearance for practical applications, metals are usually combined to form alloys. Therefore, in order to recover metals effectively from scrap, it is necessary to understand the leaching behavior of metals from their alloys. Many investigations on the dissolution behavior of gold and silver in alkaline cyanide solutions, and on the cathodic reduction of oxygen on gold and silver have been carried out by researchers with different approaches.²⁻¹⁷⁾ Mechanisms involved in the dissolution of these individual noble metals from their elemental states have been studied and the results have been documented,¹⁸⁻²¹⁾ but the dissolution behavior of

these metals from their alloys has not been well understood.

To delineate the electrochemistry and leaching kinetics of gold-silver alloys in aerated cyanide solution, the overall leaching reaction as well as the anodic and cathodic reactions for alloys of different compositions have been studied separately using rotating disc electrodes. The variables studied included oxygen partial pressure, rotating speed of the disc, concentration of cyanide, temperature and composition of the alloys. The dissolution potential and the rate of dissolution were obtained in view of the anodic and cathodic current-potential relationships. The results were discussed in terms of the mixed potential theory.

2. Experimental

Leaching tests were carried out in a 1000 ml Pyrex vessel placed in a water bath to keep a desired temperature. The leaching solution was prepared with analytical grade chemicals and deionized water. Sodium cyanide was used as a complexing agent and sodium hydroxide was used to adjust the pH of the solutions, while oxygen was used as an oxidant. Samples of the solution were withdrawn at regular

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time intervals for chemical analysis. All chemical analysis were carried out using Perkin Elmer Atomic Absorption Spectrometer, Model 5500.

An EG & G Princeton Applied Research (PAR) Potentiostat/Galvanostat Model 273A and Rotating Disk Electrode Model 616 were used to obtain polarization data. The potentiostat was controlled by a Model 352 SoftCorr™ II Corrosion Measurement Software. Experiments were carried out in a one liter EG & G PARC corrosion vessel Model K47. The system assembly was discussed in earlier studies.^{6,22} Sodium sulfate was used as supporting electrolytes. A saturated calomel electrode was used as a reference electrode, which was housed in a glass bridge with a Vycor tip very close to the disc surface. The current interrupt IR drop compensation mode was used throughout the experiments.

To produce the alloys, pure silver (99.9%) and pure gold (99.9%) powders with predetermined quantities were mixed and heated to about 1500°C. The molten liquid mixture was poured into a cylindrical mold followed by air quenching. Thin metal discs were cut out from these cylinders and annealed at about 750°C. The dimensions of the discs were 24.13 mm in diameter and 1 mm in thickness. The chemical compositions of these discs were confirmed by chemical analysis using an atomic absorption spectrophotometer. The compositions of the sample discs are shown in Table 1. Before every experiment, the sample disc was polished with 1 μm alumina powder and washed with deionized water and alcohol.

For the anodic studies, the solutions were purged with nitrogen gas before and throughout the experiments to eliminate the effect of oxygen. While for the cathodic studies and the leaching experiments, a

Table 1. Chemical compositions of Au/Ag alloys used in this study

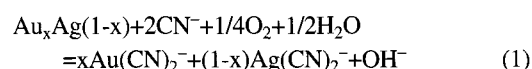
	Au At. %	Ag At. %
Sample 1		100
Sample 2	8.8	91.2
Sample 3	26.7	73.3
Sample 4	50.4	49.6
Sample 5	100	

mixture of oxygen-nitrogen gas with a pre-determined ratio was introduced into the solution to provide desired supply of oxygen.

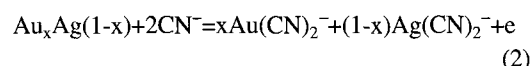
3. Results and Discussion

3.1. Electrochemical Studies

The dissolution of alloy, $Au_xAg(1-x)$ in aerated cyanide solutions can be described as follows:



This overall reaction can be separated into two electrochemical components representing the anodic oxidation of the alloy,



and the cathodic reduction of oxygen,



The anodic oxidation of the alloys at various cyanide concentrations and rotating speeds has been studied. It was found that the anodic dissolution of pure silver (Fig. 1) and Au/Ag alloys (Fig. 2) initially increased

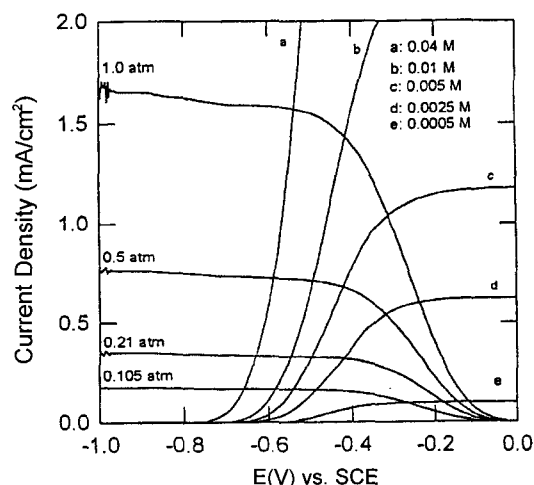


Fig. 1. Combination of cathodic and anodic polarization curves for Sample 1 (100% Ag) at various oxygen partial pressures and cyanide concentrations. Temperature: 25°C, pH 11.0, disc-rotation speed: 450 rpm, Na_2SO_4 : 0.5 M.

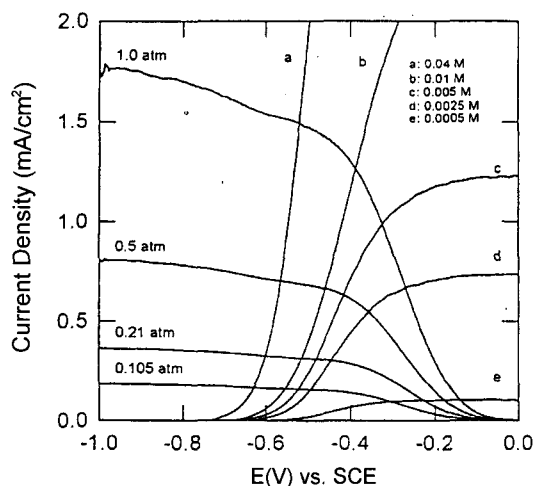


Fig. 2. Combination of cathodic and anodic polarization curves for Sample 3 (26.7% Au) at various oxygen partial pressures and cyanide concentrations. Temperature: 25°C, pH 11.0, disc-rotation speed: 450 rpm, Na₂SO₄: 0.5 M.

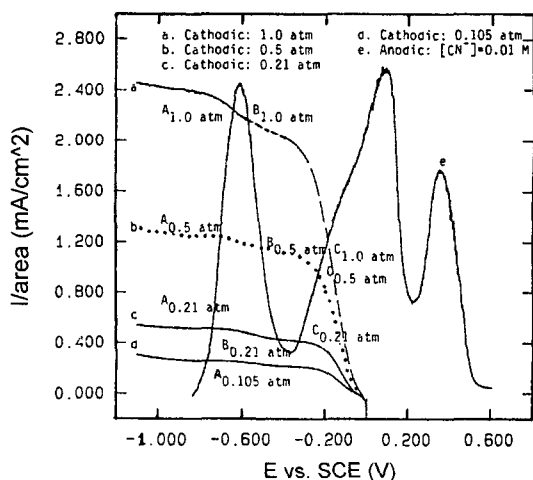
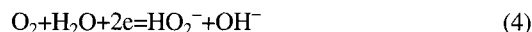


Fig. 3. Combination of cathodic and anodic polarization curves for Sample 5 (100% Au) at various oxygen partial pressures and cyanide concentrations. Temperature: 25°C, pH 11.0, disc-rotation speed: 450 rpm, Na₂SO₄: 0.5 M.

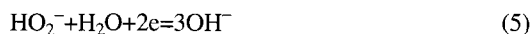
with the increase of the overpotential, and then stayed nearly constant exhibiting a limiting current. For pure gold (Fig. 3), there were three peaks observed in the potential range studied. The anodic behavior of pure silver and alloys are very similar to each other. The limiting current density increased with the increase of

the cyanide concentration and with the increase of the disc rotating speed. It followed a first order reaction with respect to the cyanide concentration, and was directly proportional to the square root of the disc rotating speed. The limiting current densities corresponding to each cyanide concentration and the disc rotating speed are in good agreement with the values predicted by the Levich's equation for a rotating disc.²³⁾

The cathodic reduction of oxygen on each sample at various oxygen partial pressures and disc rotating speeds was studied. It was found that the cathodic reduction of oxygen on these samples was a complex electrochemical process due to the nature of the electrode material. The curves (Fig. 1-3) are not single waves representing a direct 4e transfer per oxygen as indicated by Equation 3. A pathway involving two electron transfer,



may coexist with the four electron pathway according to Equation 3.⁶⁾ As a result, the cathodic polarization curves demonstrate a shape of two stages. HO₂⁻ is further reduced to hydroxyl, as shown by the following equation



As the gold concentration in the alloy increases, the difference between these two stages increases. The limiting current densities for various rotating speeds are in good agreement with the Levich's equation.²³⁾ With the increase of the oxygen partial pressure, the cathodic limiting current density increases proportionally, and follows a first order with respect to the oxygen partial pressure.

According to the mixed potential theory, the overall reaction of the dissolution of gold and silver alloys in aerated cyanide solutions can be examined by combining the anodic and cathodic current-potential curves. The current density and the potential corresponding to the interception of these two curves represent the overall dissolution rate and the dissolution potential. The location of the intersection point on both anodic and cathodic curves can reveal the mechanism of the dissolution process. The typical combinations of the anodic and cathodic curves are

also shown in Fig. 1 through 3.

It can be seen from Fig. 1 and 2 that for pure silver and gold-silver alloys the location of the intersection point is dependent on the concentration of cyanide, oxygen partial pressure and the ratio of the concentration of cyanide to that of oxygen in the solution. Three cases are considered:

Case one is at high cyanide concentrations, e.g. higher than 0.01 M. The anodic and cathodic curves intersect in the first stage region of the cathodic curves, and in the activation region of the anodic curves. This implies that oxygen becomes the limiting reactant compared with cyanide, and the reaction rate is independent on the cyanide concentration, but dependent on the oxygen partial pressure in this case. The reaction product of oxygen may contain some peroxide.

Case two is at low cyanide concentration, e.g. 0.0005 M. The intersection points are in the activation potential region on the cathodic curves, and in the concentration potential region on the anodic curve. This indicates that under the experimental conditions, cyanide and not oxygen is the limiting reactant, and the dissolution of Au/Ag alloys should be diffusion controlled by cyanide.

For case three, the intersection points are located in the transition region on both anodic and cathodic curves. This indicates that the dissolution should be mixed controlled.

The dissolution potential increased with the increase of the oxygen partial pressure at constant concentration of cyanide, and decreased with the increase of the concentration of cyanide at constant oxygen partial

Table 2. The reaction orders with respect to oxygen partial pressure for different samples. Temperature: 25°C, pH 11.0, disc-rotation speed: 450 rpm, NaCN: 0.04 M, Na₂SO₄: 0.5 M

Sample No.	Electrochem. Study	Leaching Experiments	
		Ag Component	Au Component
1	1.02 ± 0.03	1.00 ± 0.04	
2	0.99 ± 0.00	0.85 ± 0.01	0.77 ± 0.05
3	0.99 ± 0.00	0.84 ± 0.02	0.73 ± 0.04
4	0.96 ± 0.01	0.83 ± 0.04	0.64 ± 0.02
5			

pressure. The intersection points have been determined from the graphs. Table 2 lists the slopes of log (current density at the intersection point) versus log (PO₂) for different samples at [CN⁻]=0.04 M. These slopes, representing the theoretical reaction order with respect to the oxygen partial pressure, are very close to 1.

The intersection points from the combination of the anodic and cathodic current-potential curves at various disc rotating speeds were also measured for each sample. The results are plotted as log (current density at the intersection point) versus log (ω), as shown in Fig. 4. From these plots, it can be seen that a linear relationship exists between log (current density) and log (ω). The slopes of these plots are listed in Table 3. For pure silver, the slope is 0.48 which is very close to 0.5, indicating that the dissolution of pure silver is very likely mass transfer controlled under the experimental conditions. For alloys, the slope range from 0.38 to 0.44, which means that the process for alloys is mixed controlled.

The combination of cathodic and anodic polarization curves for pure gold (Fig. 3) shows that when the oxygen partial pressure is 0.105 atm, there is only one point, A_{0.105atm}, at which the total rate of oxidation and the total rate of reduction are equal. When the oxygen partial pressure is equal to or greater than

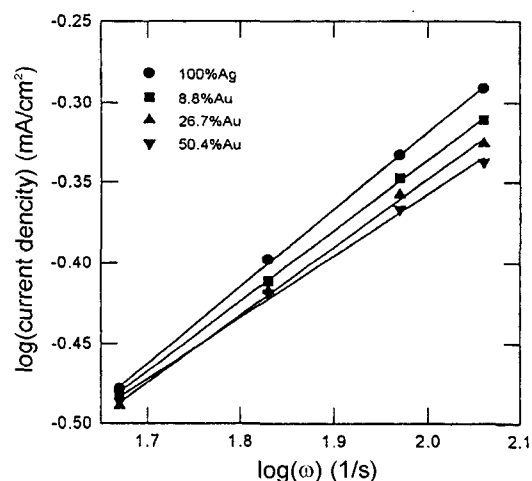


Fig. 4. Log-log plots of dissolution current density at the intersection point versus disc-rotation speed. Temperature: 25°C, pH 11.0, PO₂: 0.21 atm, NaCN: 0.04 M, Na₂SO₄: 0.5 M.

0.21 atm, there are three intersection points at which the total rate of oxidation and the total rate of reduction are equal for each oxygen partial pressure value. These results indicate that the dissolution of pure gold will be inhibited by the passivation of gold surface in the aerated cyanide solutions when the oxygen partial pressure is equal to or greater than 0.21 atm.

3.2. Leaching studieies

3.2.1. Effect of oxygen partial pressure

According to the results of electrochemical studies, when cyanide is excessive, the oxygen becomes the limiting reactant. In order to confirm the effect of oxygen of the leaching processes, the samples were subjected to leaching at different oxygen partial pressures above the solution surface, which were 0.105, 0.21, 0.5, and 1.0 atm, respectively. The results obtained are presented in Fig. 5 for silver and gold component.

For pure silver and silver component in the alloys, the log (rate) versus log (P_{O_2}) plots show that alloys of different compositions have different slopes. With the increase of oxygen partial pressure, the leaching rate

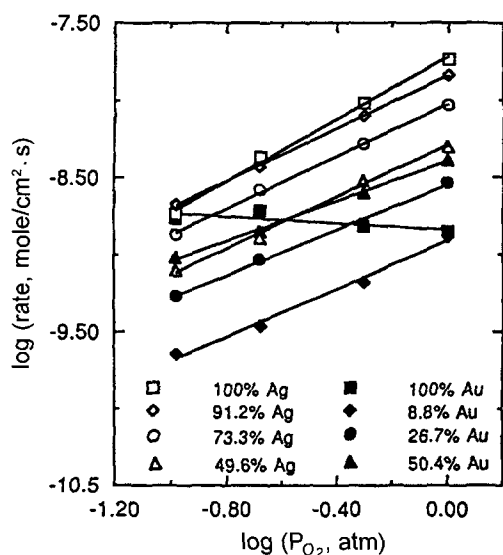


Fig. 5. Log-log plots of the silver and gold dissolution rate versus the oxygen partial pressure. Temperature: 25°C, pH 11.0, disc-rotation speed: 450 rpm, NaCN: 0.04 M.

increases accordingly. The slopes calculated for silver and gold components are also listed in Table 2. It can be seen from Table 2 that the reaction orders with respect to the oxygen partial pressure from the leaching experiments are consistent with that obtained from the electrochemical studies.

3.2.2. Effect of rotating speed

If a leaching process is mass transfer controlled or mixed controlled, the leaching rate will be affected by the disc rotating speed. The results of log (rate) versus log (ω , angular velocity) are shown in Fig. 6 for both silver and gold. For silver and its alloys, the log (rate) versus log (ω) plots show that alloys of different compositions have different slopes and their values are also listed in Table 3. From these values, we can see that for pure silver the slopes from the electrochemical study as well as from the leaching experiments are very close to 0.5 indicating that the leaching process of pure silver under the experimental conditions is likely mass transfer controlled. The values of the slopes for silver and gold components in the alloys are ranging from 0.27 to 0.43, indicating that the dissolution process for Au/Ag alloys is mixed controlled—largely by mass transfer, but partially by chemical reaction on the alloy surface.

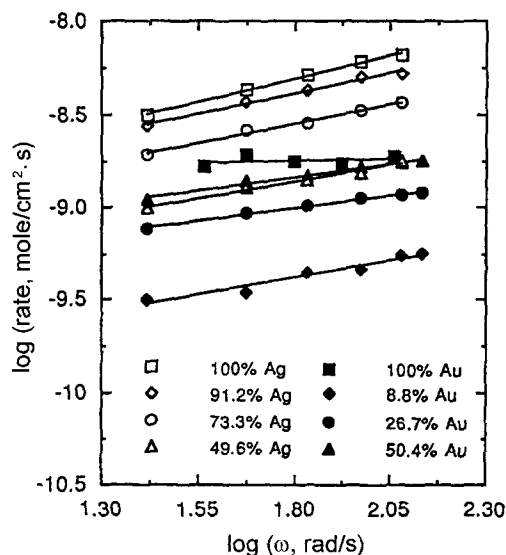


Fig. 6. Log-log plots of the silver and gold dissolution rate versus the disc-rotation speed. Temperature: 25°C, pH 11.0, P_{O_2} : 0.21 atm, NaCN: 0.04 M.

Table 3. The slopes of log (current density) vs. log (ω) for different samples. Temperature: 25°C, pH 11.0, PO₂: 0.21 atm, NaCN: 0.04 M, Na₂SO₄: 0.5 M

Sample No.	Electrochem. Study	Leaching Experiments	
		Ag Component	Au Component
1	0.48 ± 0.01	0.49 ± 0.03	
2	0.44 ± 0.00	0.43 ± 0.03	0.39 ± 0.05
3	0.42 ± 0.01	0.42 ± 0.02	0.27 ± 0.01
4	0.38 ± 0.01	0.37 ± 0.03	0.29 ± 0.02
5	N/A		0

3.2.3. Effect of cyanide concentration

The effect of cyanide concentration on the leaching rate of silver and gold from the alloys was studied. It was found that when cyanide concentration was less than 0.001 M, the leaching rate increased with the increase of the cyanide concentration. The reaction order with respect to cyanide concentration was found to be about 0.9. When cyanide concentration was greater than 0.001 M, however, the leaching rate was found to be independent of cyanide concentration. The results observed here are in line with that predicted in the electrochemical study.

3.2.4. Effect of temperature

The effect of temperature on the leaching rate of the alloys was investigated by measuring the leaching rates at different temperatures. The activation energies were obtained from the plots of log (rate) versus 1/T plot. It is necessary to note that the oxygen solubility in aqueous solution is dependent on temperature, so a correction factor should be introduced. Therefore, the results from the experiments are plotted as log ((0.0617 × T - 14) × rate) versus 1/T × 1000.²⁴⁾ The activation energy values calculated from the plots are listed in Table 4. From Table 4 it can be seen that the activation energies of silver component are in the range of 19.31 to 31.81 kJ/mole (4.62 to 7.61 kcal/mole) which are compared with 15.68 kJ/mole (3.75 kcal/mole) for pure silver. These results support the proposed mechanism in which the leaching process of pure silver is mass transfer controlled while that of silver component from the alloys is mixed controlled. The activation energies of gold component are in the

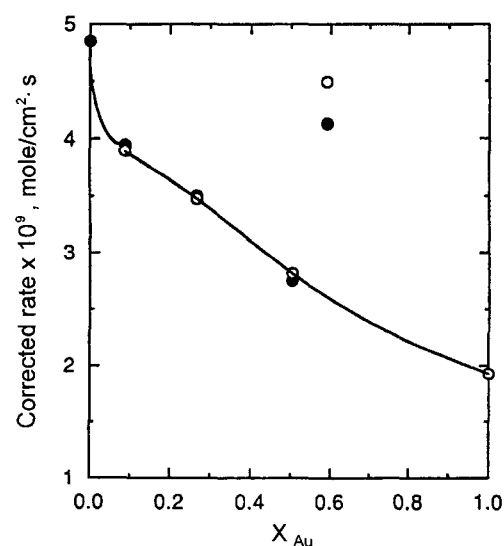
Table 4. Activation energies (kJ/mole) for gold, silver and their alloys at 15-55°C, unless stated otherwise

Sample No.	Ag Component	Au Component
1	15.68 ± 0.59	
2	19.31 ± 0.50	22.57 ± 1.87
3	23.53 ± 0.75	23.83 ± 1.34
4	31.81 ± 0.59	28.93 ± 1.92
5		60.23 ± 11.87 (15-35°C) 21.86 ± 2.51 (35-65°C)

range of 22.57 to 28.93 kJ/mole (5.40 to 6.92 kcal/mole). This result indicates that the leaching process of gold component from alloys is likely to be mixed controlled, which is different from pure gold.

3.2.5. Effect of alloy composition

In order to compare the dissolution rate of an individual element to that of a pure metal system, the dissolution rates of metals from their alloys were corrected according to the number of atoms per unit area. Fig. 7 shows the effect of alloy composition on the dissolution rate of metals from alloys. It can be

**Fig. 7.** Effect of alloy composition on the corrected dissolution rate of gold-silver alloys. Temperature: 25°C, pH 11.0, PO₂: 0.21 atm, NaCN: 0.04 M, disc-rotation speed: 450 rpm.

seen that the corrected gold dissolution rate of alloys was higher than that of pure gold due to the formation of passivation film on the surface. The corrected dissolution rates of silver from alloys were lower than that of pure silver due to a greater chemical bond strength and higher activation energy. Also, as mentioned in the electrochemical studies, the cathodic reduction of oxygen on these samples was a complex electrochemical process. With the increase of gold content in the alloy, the cathodic reaction of oxygen takes place more according to two electron transfer, resulting lower dissolution rate.

4. Conclusions

The overall dissolution reaction was examined by combining the anodic and cathodic current-potential curves. It was found that the dissolution rate of pure silver and Au/Ag alloys was limited by transport of either oxygen or cyanide, depending on their relative concentration, in some cases it was mixed controlled. When cyanide was the limiting reactant, the reaction order with respect to cyanide was found to be about 0.9. When oxygen was the limiting reactant, the dissolution rate was proportional to the $PO_2^{0.7-1}$. The rate increased with the increase of the disc rotating speed according to a 0.3 to 0.5 order. The activation energies for the dissolution were found to be in the range of 15.68 to 31.81 kJ/mole (3.75 to 7.61 kcal/mol). The corrected gold dissolution rate of alloys was higher than that of pure gold, and the corrected dissolution rates of silver from alloys were lower than that of pure silver.

Acknowledgments

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