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CANADA
DEPARTMENT OF MINES AND TECHNICAL SURVEYS
MINES BRANCH

ELECTRODE POTENTIALS
and
THE DISSOLUTION OF GOLD

by

G. Thomas

MINERAL DRESSING AND PROCESS METALLURGY DIVISION



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A faint, large watermark is visible in the background of the page. It appears to be a technical diagram or schematic related to mineral processing, possibly showing a cylindrical vessel or a similar piece of equipment.

ELECTRODE POTENTIALS AND THE DISSOLUTION OF GOLD.

Research Report No. MD172

By

G. Thomas*

INTRODUCTION

From time to time since the advent of the cyanide process, the use of electrode potentials for testing cyanide solutions has been advocated. This is perhaps due in part to the relative simplicity of obtaining electrode potentials. Electrode potentials may be measured readily with an ordinary pH meter modified by replacing the glass electrode by a metal electrode.

Several reports have indicated that a modified pH meter would be valuable for cyanide mill operators. As early as 1880⁽¹⁾, Gore found that the dissolution rates of various metals in KCN solutions showed close agreement with the electrode potentials of metals in cyanide solutions. A greater electrode potential was reflected by a greater rate of dissolution. Christy⁽²⁾ in 1900 found that electrode potential curves and dissolution rate curves of gold in various cyanide solutions showed an apparent correlation. John and Beyers⁽³⁾ state that the modified pH meter is a "practical means of measuring the efficiency or activity of cy-

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anide solutions to dissolve gold". Beyers⁽⁴⁾, using a modified pH meter and a flowing cyanide solution, concluded that "an apparent correlation exists between the rate of dissolution and the corresponding electrode potential of pure gold".

More recently, Thompson⁽⁵⁾ used a modified pH meter with a recorder to investigate the dissolution of gold in cyanide solutions. In his paper Thompson states: "The electrochemical technic provides a means of assessing those factors which chemical analysis fails to do in many cases. Thus the active concentration of the cyanide ions is a quantity which may vary considerably without the total KCN percentage composition altering, and again the influence of oxygen is given a more quantitative standing than that obtained by the somewhat difficult and rarely executed chemical determination. Another advantage of the method is that it is possible to evaluate these factors at any point in the pulp or solutions instantaneously and to make an autographic record of the conditions of the solutions continuously and with the same facility as the temperature of a furnace may be recorded. "

From the various reports mentioned, an instrument to record electrode potentials would appear to be extremely useful to cyanide mill operators. However, a brief experimental investigation, together with a study of the electrochemical principles involved in the dissolution of gold, indicates that such an instrument would be unsatisfactory for cyanide solution control.

EXPERIMENTAL RESULTS

The apparatus shown in Fig. 1 was used to obtain the electrode potentials of gold and silver, or, more strictly, the potential differences between the metal electrode and the saturated calomel electrode. A flowing solution was used to ensure the electrodes being surrounded by fresh solution at all times, and a high solution velocity of 1000 cm. /min. prevented changes in electrode potentials from minor variations in flow rate.

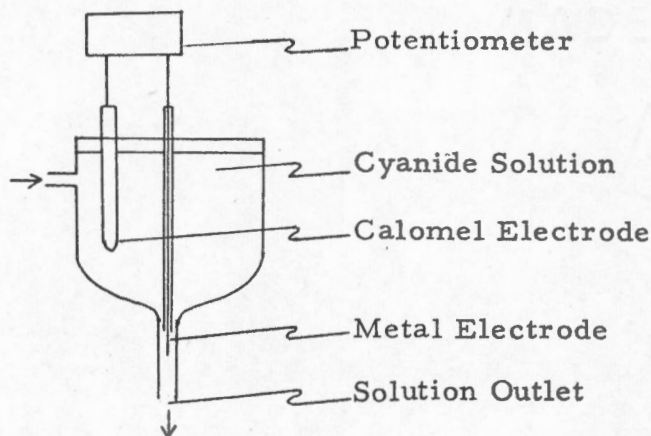


Fig. 1. Modified pH Meter and Flowing Solution Cell.

Several aerated cyanide solutions containing up to 2 lb. NaCN/ton and up to 1 lb. CaO/ton were prepared and the pH of each solution was measured. Using the modified pH meter with a silver electrode, the solution was allowed to flow until the potential difference between the silver electrode and the saturated calomel electrode became constant. This required the passage of approximately 10 litres of solution. The procedure was repeated for each cyanide solution with the results shown in Fig. 2.

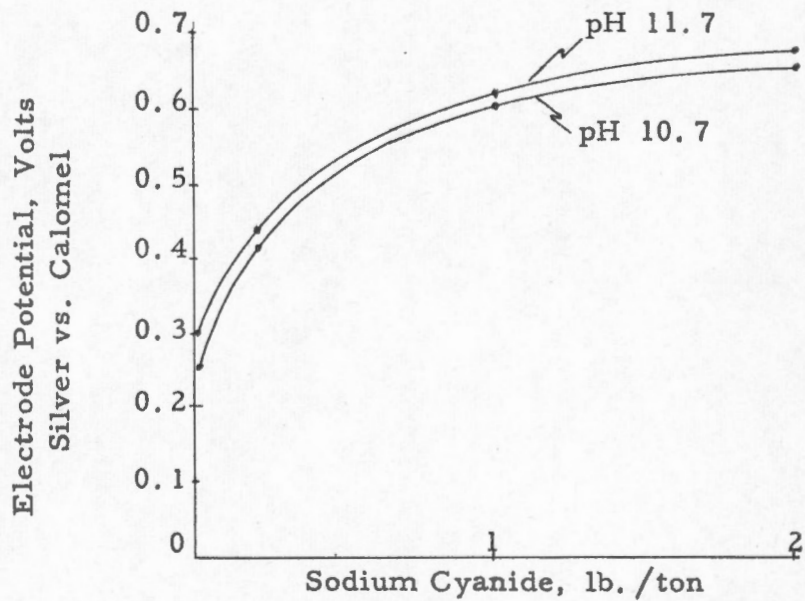


Fig. 2. Effect of Cyanide Concentration and pH on Electrode Potential.

It is quite possible that curves similar to either of those shown in Fig. 2 were used by previously mentioned authors recommending the electrochemical method of testing cyanide solutions. The

curves show that cyanide concentrations can be determined from electrode potentials with the rigid requirement being that the cyanide concentration be the only variable present. However, cyanide solutions normally contain other variables. As clearly shown in Fig. 2, the electrode potential is also affected by the pH. Hence, in cyanide solutions of varying pH the cyanide concentration cannot be obtained from the observed potential.

Furthermore, electrode potentials are of no value in determining the gold-dissolving activity of cyanide solutions. Figure 2 shows that the electrode potentials continue to increase with increasing cyanide concentrations. On the other hand, the rate of dissolution of gold increases only to a certain maximum with increasing cyanide concentration; depending on aeration, etc., this optimum cyanide concentration has been variously stated⁽⁶⁻⁸⁾ to be from 0.26 to 1.0 lb. NaCN/ton. Figure 2 also shows that an increase in alkalinity increases the electrode potential. But increases in alkalinity, particularly when the alkalinity is due to lime⁽⁸⁾, actually decrease the rate of gold dissolution in cyanide solutions. It is evident, therefore, that electrode potentials cannot be used to obtain the activity of a cyanide solution for dissolving gold.

In addition to pH and cyanide concentration, cyanide solutions vary in the amounts of dissolved oxygen, silver and gold, each of

which affects electrode potentials. For example, the potential of a silver electrode vs. a calomel electrode in an aerated solution containing 0.2 lb. NaCN/ton was found to be 0.40v. After deaeration of the solution the potential increased to 0.50v., i. e. the removal of oxygen has the same effect as an increase in cyanide concentration on electrode potential. The addition of silver nitrate to the aerated solution to give 0.3 ounce dissolved Ag/ton lowered the potential to 0.34v., i. e. for solutions of the same cyanide concentration the electrode potential is lower in a pregnant solution than in a barren solution.

Cyanide solutions used in mill operations are likely to contain many substances which affect electrode potentials. In the laboratory, the potential of a gold electrode vs. a calomel electrode in an aerated solution containing 1 lb. NaCN/ton and 0.1 lb. CaO/ton was found to be 0.49v. To separate portions of this solution, thiocyanate, ferrocyanide and ferricyanide were added to give molar concentrations 1.5 times greater than that of the cyanide. In these solutions the potentials of the gold electrode were 0.52v., 0.54v. and 0.27v., respectively. In such solutions, therefore, electrode potentials would be useless for determining cyanide concentrations.

The additions of thiocyanate and ferrocyanide increased the potential of the gold electrode just as an increase in cyanide concentration would have done. However, thiocyanate and ferrocyanide have little effect⁽⁹⁻¹¹⁾ on the rate of dissolution of gold. Further, while ferri-

cyanide considerably decreased the potential of the gold electrode, ferricyanide greatly increases⁽¹¹⁾ the rate of dissolution of gold in cyanide solutions.

Solutions used in cyanide mill operations contain many substances which affect electrode potentials. Because of this, electrode potentials cannot be used to measure either the cyanide concentration or the gold-dissolving activity of cyanide mill solutions.

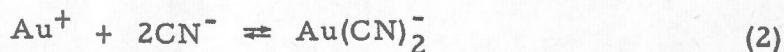
DISCUSSION

Electrochemical theory provides a ready interpretation of the experimental results which have just been described. When a gold electrode, which consists simply of a gold wire, is placed in pure water, the gold starts to dissolve according to

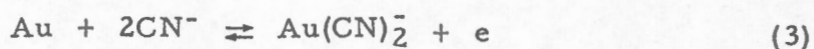


When gold ions enter the water, the metallic gold becomes negatively charged due to accumulation of electrons. As this process continues, the positively charged gold ions find increasingly greater difficulty in escaping from the metallic gold. An equilibrium is quickly set up in which forward and reverse reaction rates become equal to one another and dissolution ceases.

In the presence of cyanide ions, the concentration of positively charged free gold ions is greatly reduced by formation of aurocyanide ions.



This removal of free gold ions in solution allows more gold to dissolve by reaction (1) until a new equilibrium is established. Combination of reactions (1) and (2) gives

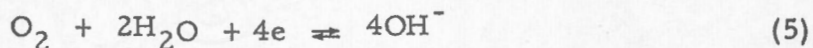


The accumulation of electrons resulting from the anodic reaction (3) gives the gold wire or electrode a certain charge or potential. The value of this potential is commonly expressed in relation to that of the standard hydrogen electrode which has an arbitrarily assigned value of 0.00v. According to Latimer⁽¹²⁾, for reaction (3), the potential of a gold electrode in a cyanide solution containing 1 mole of cyanide and aurocyanide ions/kgm. water is 0.60v. At any other concentration the potential of the gold electrode is given by

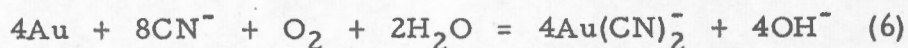
$$E = 0.60 - 0.059 \log \frac{[\text{Au}(\text{CN})_2^-]}{[\text{CN}^-]^2} \quad (4)$$

where for dilute solutions the quantities in square brackets represent the concentration in moles/kgm. water. The potential of a gold electrode will therefore increase with the cyanide concentration but decrease with the amount of dissolved gold.

As is well-known, oxygen is necessary for the dissolution of gold. The role of oxygen is to remove electrons from the gold, formed by reaction (3), by the cathodic reaction (5) and thus permit the dissolution to continue.

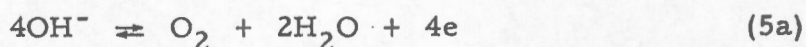


Addition of reactions (3) and (5) gives the well-known equation for the dissolution of gold.



Thus, dissolution of gold is simply the formation of gold ions and the complexing of these ions by cyanide to give the metallic gold a negative charge. Oxygen removes this charge and allows gold dissolution to continue. This electrochemical nature of gold dissolution has frequently (2, 5, 6) been reported in the literature.

In electrode potential work, the cathodic reaction (5) is usually expressed as an oxidation reaction,



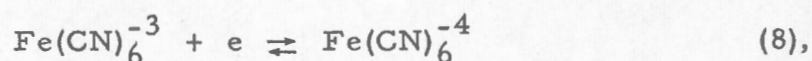
According to Latimer⁽¹²⁾ the electrode potential for this reaction, for any pH and under any pressure of oxygen in atmospheres, is given by

$$E = -1.229 + 0.059 \text{ pH} - \frac{0.059}{4} \log P_{\text{O}_2} \quad (7)$$

The electrode potential for this reaction increases with the pH and decreases with the amount of dissolved oxygen.

In an aerated cyanide solution, the anodic reaction (3) attempts to produce on a gold electrode a potential whose value is given by equation (4). At the same time, removal of electrons by the cathodic reaction (5) attempts to change the potential to that given by equation (7). As a result, some intermediate potential will be established on the electrode, namely the "observed" potential.

The cyanide concentration is not the only factor governing the observed electrode potential. As shown by equations (4) and (7), the pH and the amounts of dissolved gold and oxygen are also of great importance in establishing the electrode potential. Likewise, any substance present in the solution and capable of depositing or removing electrons from the gold, viz.



would also affect the observed potential. Hence, unless all the numerous factors, other than cyanide concentration, are kept constant the observed potential cannot be used to determine cyanide concentration.

The electrochemical nature of metal dissolution⁽¹³⁻¹⁵⁾ shows no possibility for unambiguously relating electrode potentials to the speed of gold dissolution, as can be seen by the following considerations. The anodic reaction (3) and the cathodic reaction (5) form anodic and cathodic areas on gold immersed in a cyanide solution. As a result of this, the gold functions as a galvanic or voltaic cell and produces an electric current, called the corrosion current. The path of this current is through the gold to the anodic areas, through the cyanide solution to the cathodic areas, and back through the gold. As in other electrolytic processes, the rate at which gold dissolves anodically is proportional to this corrosion current.

In Fig. 3, the variations of the corrosion current, i. e. the rate of gold dissolution, in relation to electrode potentials is shown diagrammatically. In a given cyanide solution, the potentials of the anodic and cathodic areas may, for example, be A_1 and C_1 respectively. As a result of the potential difference existing between A_1 and C_1 , an electric current I_1 will be produced. The strength of this current will be governed, according to Ohm's law, by the potential difference and the resistance of the circuit. The observed potential, O_1 , will be somewhere intermediate between A_1 and C_1 . Should the resistance of the anodic area be smaller than that of the cathodic area, the observed potential would be closer to A_1 than to C_1 , in accordance with Ohm's law. To facilitate the discussion, the above cyanide solution is called solution 1.

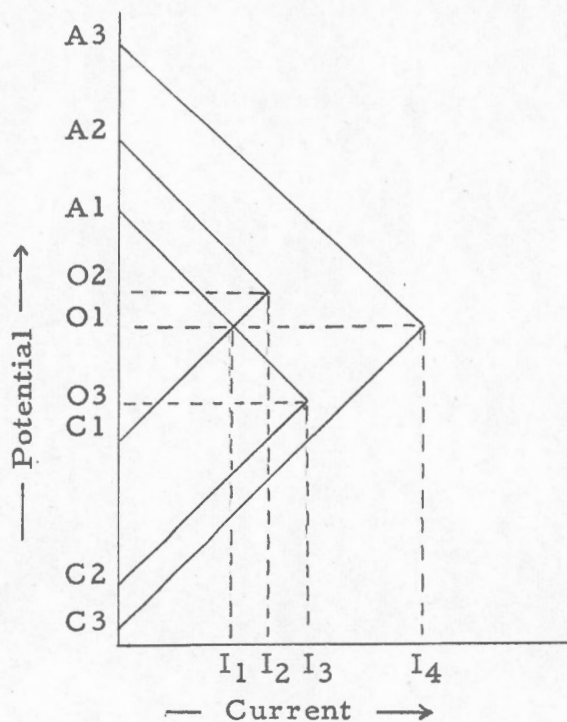


Fig. 3. Effect of Electrode Potential on Corrosion Current.

As given by equation (4), the potential of the anodic portion of the gold may be raised to A_2 by an increase in cyanide concentration or by a decrease in the amount of dissolved gold. An increase in the anodic potential to A_2 would increase the observed potential to O_2 and increase the corrosion current to I_2 . This is in agreement with the Mass Action law applied to equation (6) wherein an increase in cyanide concentration or a decrease in the amount of dissolved gold would speed up the dissolution of gold.

Instead of the anodic potential being raised, the cathodic potential may be lowered to C_2 . This may result, as given by equation (7), from a decrease in pH or from an increase in the amount of dissolved oxygen. While this lowering of the cathode potential would lower the observed potential to O_3 , the greater potential difference existing between A_1 and C_2 would actually increase the corrosion current to I_3 . The results of these changes are to be expected from an application of the Mass Action law to equation (6). In this cyanide solution, compared with solution 1, gold would show a lower observed potential but a greater rate of dissolution.

If solution 1 be replaced by some other cyanide solution, the anodic potential may be raised to A_3 and the cathodic potential may be lowered to C_3 . While this would not change the observed potential, the increased potential difference would increase the corrosion current

to I_4 . As still another case in point, should the resistance of the circuit be decreased, then, by Ohm's law, the corrosion current would increase further. Consequently, in various cyanide solutions, gold may show the same observed potential but dissolve at entirely different rates.

SUMMARY

The use of electrode potentials for measuring the activity of cyanide solutions as solvents for gold has frequently been advocated. Experimentally, the potential of a metal electrode in cyanide solutions was found to depend not only on the cyanide concentration but also on the pH, on the amounts of dissolved gold (or silver) and oxygen, and also on the presence of salts frequently found in cyanide mill solutions. The potential of a gold electrode cannot therefore be unambiguously related to the activity or the dissolving power of the cyanide solution for gold.

The dissolution of gold is discussed as an electrochemical process. The origin of the "observed" potential is described in relation to the potentials produced by the elementary reactions involved in gold dissolution. The corrosion current or the rate of gold dissolution is shown to be independent of the observed potential.

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