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MEASUREMENT OF DISSOLVED AIR IN ALKALINE SOLUTIONS FROM URANIUM MILLS AND FROM GOLD MILLS

G. THOMAS   AND   T. R. INGRAHAM

EXTRACTION METALLURGY DIVISION

DEPARTMENT OF MINES AND
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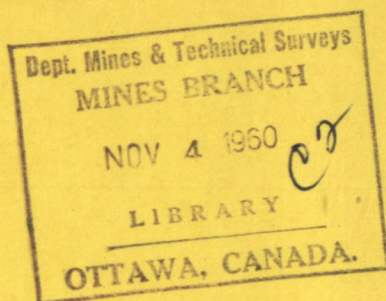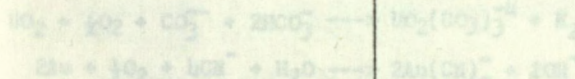Extraction Metallurgy Division

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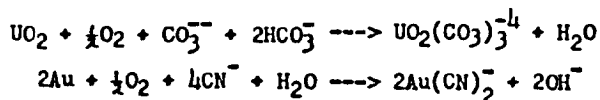
URANIUM MILLS AND FROM GOLD MILLS

by

Dr.G.Thomas and Dr.T.R.Ingraham
Extraction Metallurgy Division,
Mines Branch, Department of Mines
and Technical Surveys, Ottawa, Canada.

ABSTRACT

A simple and rapid method has been developed for determining the relative saturation of air in the alkaline solutions used in processing uranium ores and gold ores. The method is based on the diffusion current produced by oxygen from the dissolved air when a sample of the solution is subjected to a controlled potential applied to a calomel anode and a platinum cathode. Since the diffusion current is proportional to the relative saturation of air in the solution, and since only relative saturation levels are required for mill control work, it is sufficient to apply a fixed potential and to measure the diffusion currents with a microammeter.

INTRODUCTION

Oxygen obtained from dissolved air is one of the essential components in the reactions that take place in alkaline solution during the processing of some uranium ores and of gold ores. This requirement for oxygen is evident from the following typical equations:

$$UO_2 + \tfrac{1}{2}O_2 + CO_3^{--} + 2HCO_3^- \longrightarrow UO_2(CO_3)_3^{-4} + H_2O$$

$$2Au + \tfrac{1}{2}O_2 + 4CN^- + H_2O \longrightarrow 2Au(CN)_2^- + 2OH^-$$

Not all of the oxygen in the dissolved air is available for the above reactions. Some of it is consumed in the oxidation of iron sulphide minerals such as pyrite or pyrrhotite. As a result, in insufficiently aerated or poorly agitated areas of the leaching vessels, sufficient dissolved oxygen may not be available for the dissolution of the uranium minerals or the gold. This lack of oxygen leads to poor efficiencies in the leaching circuits and to decreased recoveries.

From the foregoing, it is apparent that in the interests of efficiency it would be convenient to be able to follow the degree of aeration in various parts of a leaching circuit as the dissolution of the selected constituents of the ore progresses. Unfortunately, the chemical methods [1,2,3] available for determining the

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[1] Superior numbers refer to similarly numbered references at the end of this paper.

amount of oxygen dissolved in the solutions are either relatively complex or unreliable and hence have seldom been used in routine mill operations.

In this paper, a simple method of oxygen determination, based on the diffusion current wave of oxygen, [4,5,6,7] will be described.

APPARATUS

The apparatus for the measurement of diffusion currents produced by the dissolved oxygen is shown diagrammatically in Figure 1. A No. 6 dry cell was used as a source of potential and the required fraction of its 1.5 v was selected from a 300 ohm rheostat. The current in the circuit was measured with a microammeter. To eliminate fluctuation in the readings, a 2,000 microfarad condenser was inserted in parallel with the microammeter. The potential applied across the electrodes was measured with a high resistance millivoltmeter: in these experiments, the millivoltmeter scale on a model G Beckman pH meter was used. The use of a high resistance millivoltmeter in this application is essential if the microammeter readings of the diffusion current are to be accepted as correct.

To ensure that the measured diffusion current was controlled entirely by the rate of oxygen diffusion to the cathode, a saturated calomel anode with a large surface area (4.5 sq cm) was used.

Several optional arrangements of the platinum cathode were used. In one arrangement, a 1 to 2 cm length of 0.4 mm dia platinum wire was attached to a beeswax-coated brass rod or was sealed into a glass capillary tube which was bent at a 90° angle at its tip. Electric contact with the platinum was made by filling the capillary with mercury. This electrode was rotated at a constant speed of 800 rpm. In another arrangement, the platinum electrode was kept stationary and the solution was stirred vigorously. All arrangements produced the same results.

In the preliminary experiments, it was found that the platinum cathode became polarized after use, making the measurements of diffusion currents erratic. To clean the electrode prior to making measurements, a secondary electrolytic circuit was introduced through which the cathode was made anodic for about 10 sec.

RESULTS

The initial experiments to establish the technique were done with synthetic solutions having a composition typical of those used in the uranium industry for alkaline leaching, eg 115 g Na_2CO_3 and 15 g $NaHCO_3$ per litre. When these solutions were saturated with air and subjected to an increasing potential between the electrodes, the diffusion currents obtained were typical of an oxygen wave.[4] The graph of current versus potential is shown in Figure 2, from which it is apparent that within the potential range 0.50 to 0.85 v the diffusion current was constant and was limited by the diffusion of oxygen to the cathode.

In subsequent work, a potential which would produce a constant diffusion current was selected from Figure 2 and it was held constant in experiments during which the percentage air saturation of the solutions was varied. A potential of 0.70 v was selected, and the amount of air in the test solutions was varied, by diluting an air-saturated solution with deaerated solution.

In a typical experiment, 25 ml of the Na_2CO_3-$NaHCO_3$ solution was placed in the cell and air was bubbled through it until the solution was saturated. The platinum electrode was then depolarized and a potential of 0.70 v was applied between the electrodes. After a short period the diffusion current became constant, and this constant value was considered to represent the level at saturation. At this point, 25 ml of deaerated solution was added, and the diffusion current then decreased sharply to a steady reading of just about half its former value. This is shown by the line to the right of Figure 3. When an additional amount of deaerated solution was added, duplication of the original behaviour was observed. When the diffusion currents were plotted against the percentage air saturation, the line to the left in Figure 3 was obtained. For all practical purposes this line can be considered as a linear relationship between the diffusion current and the percentage air saturation. From the foregoing results, the application of diffusion current measurements to the determination of the degree of air saturation of alkaline solutions seemed promising.

When the foregoing experiments on synthetic mill solutions were repeated with actual solutions obtained from operating uranium mills and gold mills, the same wave patterns were discernible but less distinct. Because of this, it was decided that reliable results could not be obtained by referring the diffusion currents of actual mill solutions to synthetic mill solutions. Instead, a method of referring each mill solution to its own fully aerated and deaerated state was developed.

As a point of reference for the determinations, standard solutions containing known relative amounts of dissolved air were prepared.

These standard solutions were prepared by diluting a sample of air-saturated mill solution with sufficient deaerated mill solution to give standard samples containing 25, 50, 75 and 85 percent of the amount of air required for saturation. This was done both for uranium mill solutions and for gold mill solutions. These two groups of standard solutions were then used in determinations of percentage air saturation by diffusion current measurements. The procedure was as follows:

A sample of air-saturated mill solution was placed in the beaker containing the electrodes, and the potential between the electrodes was adjusted to 0.70 v and maintained there for about 20 min or until the diffusion current was constant. During this period, the electrodes became conditioned and were ready for actual comparison measurements. In the first step of the comparison, the conditioning solution was replaced quickly by one of the standard mill solutions and the diffusion current was read immediately after the replacement. In the second step, this procedure was repeated with a fresh sample of aerated solution, to obtain its diffusion current, and after the reading had been made the solution was purged with nitrogen to remove the oxygen. The diffusion current of this purged solution was then read and its value subtracted from that obtained for the standard solution and that obtained for the air-saturated solution. The ratio of these remainders, multiplied by 100, was considered to represent the percentage air saturation of the solution. To show the success of this simple method, a comparison is made, in Table 1, of the standard air saturations with the measured air saturation for uranium mill and gold mill solutions.

TABLE 1

Determination of % Air Saturation by Diffusion Currents

% Air Saturation (prepared standards)	% Air Saturation (determined by diffusion currents)	
	U mill soln.	Au mill soln.
25	29	30
50	52	58
75	76	80
85	86	84

From Table 1, it is evident that diffusion current measurements can be used for the determination of air saturation and that the accuracy of the percentage air saturation determinations in uranium mill solutions is somewhat better than that for gold mill solutions. However, since

differences in aeration of about ten percent are
not likely to be significant in actual operation,
the results would seem to be quite acceptable
as a control measure for operating mills.

CONCLUSIONS

From simple measurements of diffusion cur-
rents at a constant applied potential, it has
been shown that the diffusion currents in actual
uranium mill and gold mill solutions are pro-
portional to the percentage air saturation of
the solutions.   This conclusion has been uti-
lized to develop a simple instrumental measure-
ment that can be used as a control measure in
operating uranium mills and gold mills.

REFERENCES

1. Hamilton, E.M., "Manual of Cyanidation",
    McGraw-Hill Book Co. Inc., New York (1920).

2. Weinig, A.J., and Bowen, M.W., Trans. Am.
    Inst. Mining Met. Engrs., 159, 227 (1944).

3. Furman, N.H., "Scott's Standard Methods of
    Chemical Analysis", 5th Ed., D. Van Nostrand
    Co., New York (1939).

4. Kolthoff, I.M., and Lingane, J.J., "Polar-
    ography", 2nd Ed., Interscience Publishers,
    New York (1952).

5. Marsh, G.A., Analyt. Chem., 23, 1427 (1951).

6. Armstrong, F.E., Heemstra, R.J., and Kincheloe,
    G.W., Analyt. Chem., 27, 1296 (1955).

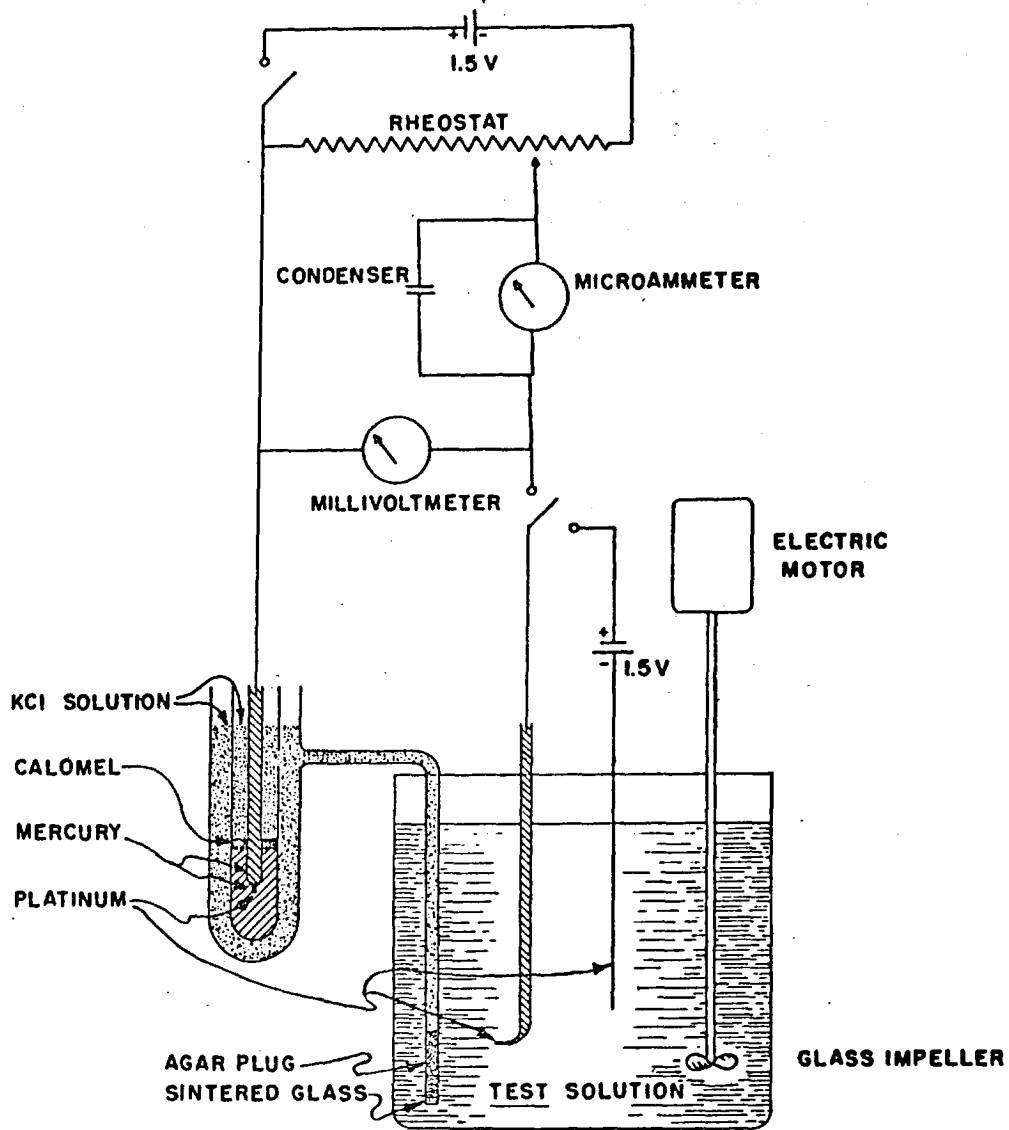7. Warshowsky, B., and Schantz, E.J., Analyt.
    Chem., 26, 1811 (1954).

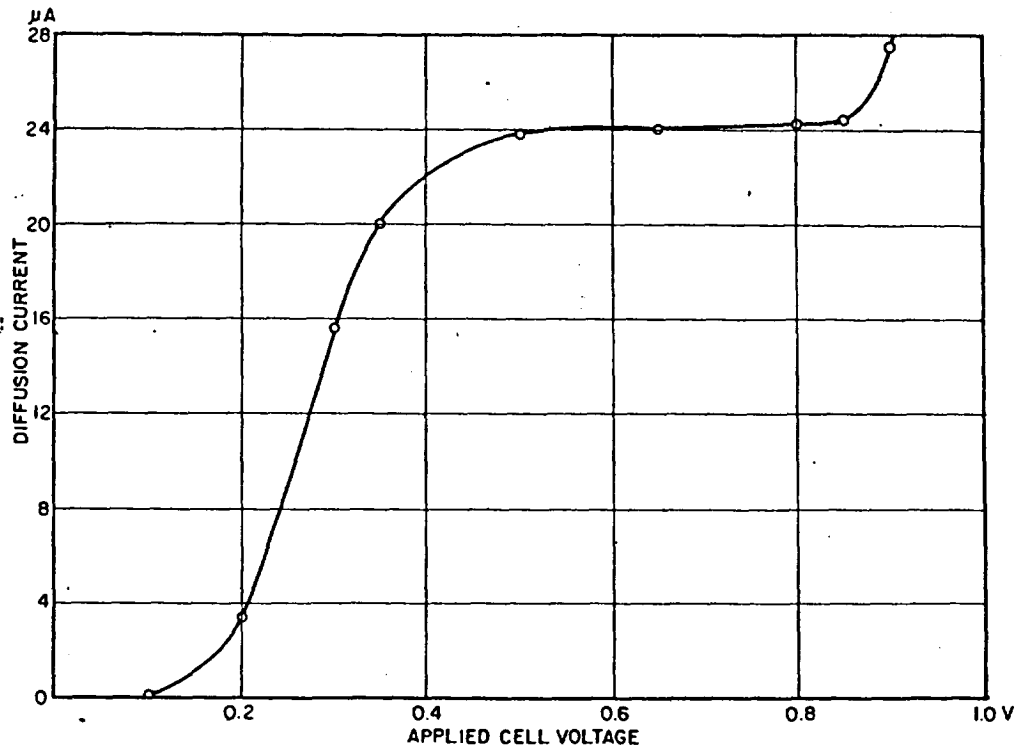FIG. I- DIAGRAM OF DISSOLVED OXYGEN METER.
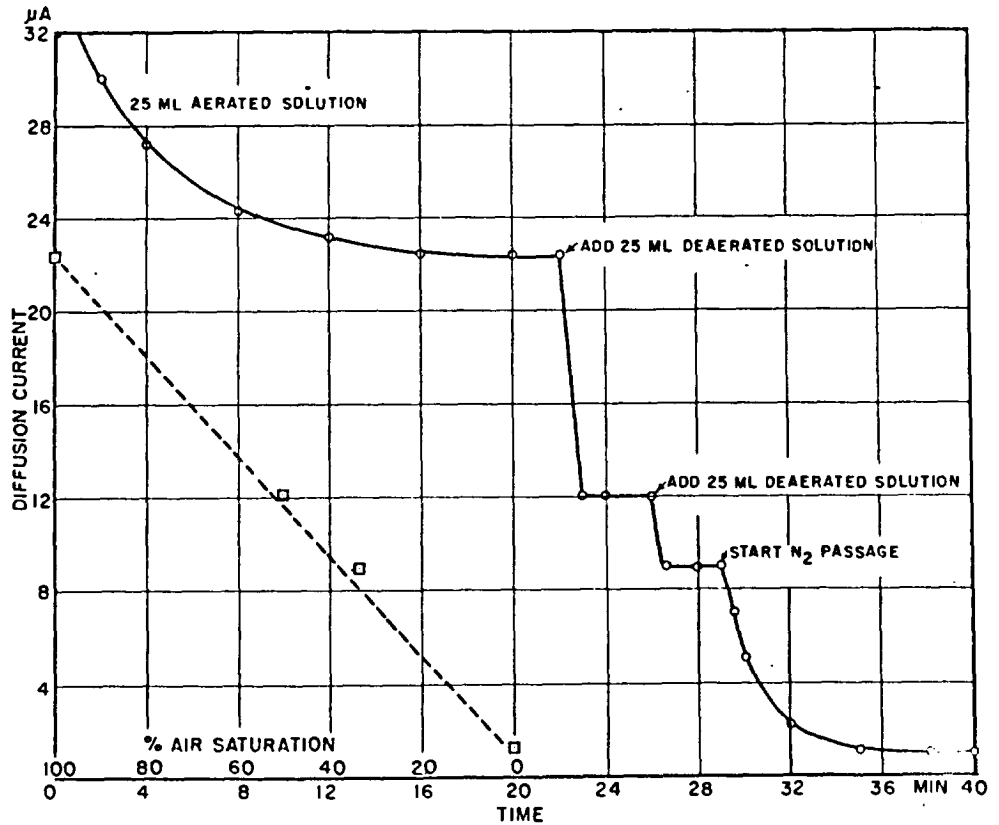
FIG. 2 - EFFECT OF CELL VOLTAGE ON DIFFUSION CURRENT.

FIG. 3 - EFFECT OF AERATION ON DIFFUSION CURRENT.