Study of Precipitation of Copper on Iron from Acid Solutions

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THE REGENTS

Introduction

Copper is leached from low-grade mine dumps and caved cap rock in increasing amounts in the Southwest United States mining industry. The red metal is recovered as cement copper by precipitation on iron, usually tin-can scrap. This activity is very important to the copper mining industry because cement copper is the cheapest copper it produces, assuming, of course, that the cost of mining the waste to be leached can be charged legitimately to the usual mining and milling operations. Production of cement copper has increased steadily, particularly during recent years, until it now accounts for several per cent of the total Southwest copper output (Beall, 1965).

This study is part of an attempt to elucidate the principles of the cementation process in some detail and to search for the optimum chemical and hydrodynamic conditions for precipitation of copper by cementation on iron. It started with the hypothesis that, in the acid leach solutions encountered in the industry, the iron used for precipitation is polarized with a film of hydrogen in some unspecified activated state and that subsequent reaction of cupric ion with this activated hydrogen accounts for at least part of the copper precipitated at the iron surface, the fraction depending upon concentrations of reacting ions in the leach solutions and the hydrodynamic conditions prevailing.

It is reasoned that depletion of copper from the leach solution at the metal-solution interface offers the opportunity for reduction of hydrogen ion by the metallic iron. Some of this hydrogen is more or less slowly liberated as hydrogen gas and escapes to the atmosphere; some of it is oxidized by cupric ion while it is still in the activated state. The rate of diffusion of hydrogen ion to the interface is large compared to the diffusion rates of other ions in leach solutions because of its relatively high concentration and its large diffusivity. Consequently, there will always be hydrogen on the iron surface, some of it in the process of transforming to hydrogen molecules. The amount of hydrogen escaping from the system as molecules represents non-productive consumption of iron. Possibly this part of the total iron consumption in a cementation operation might be minimized by achieving hydrodynamic conditions that maintain the maximum flux of copper ions through the diffusion layer at the metal-solution interface. Hydrogen in the activated state, but not yet combined into molecules, might then be largely oxidized by cupric ions. The work described in this paper was performed to learn if there are obvious objections to this hypothesis. Other work is being done to find the combinations of variables that provide optimum cementation conditions.

Formation of activated hydrogen on the surface of iron and subsequent reaction with cupric ions according to the equations

$$2H^+ + Fe^0 = 2H(a) + Fe^{++} \qquad (1)$$
$$Cu^{++} + 2H(a) = Cu^0 + 2H^+ \qquad (2)$$
$$\overline{Cu^{++} + Fe^0 = Cu^0 + Fe^{+=}} \qquad (3)$$
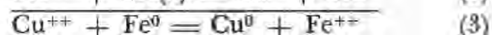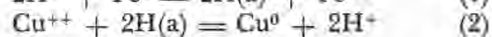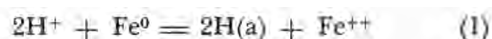
lead to the over-all reaction (3) that describes the net action between cupric ion and metallic iron. Hydrogen in the activated state deactivates to form hydrogen gas:

$$2H^+ + Fe^0 = 2H(a) + Fe^{++} \qquad (1)$$
$$2H(a) = H_2^0 \qquad (4)$$
$$\overline{2H^+ + Fe^0 = H_2^0 + Fe^{++}} \qquad (5)$$
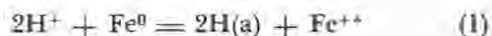
Equation (5) illustrates wasteful consumption of iron by acid in the leach solution.

Under conditions that will accelerate equation (2), more iron would be consumed in precipitating copper, as by equation (3), less iron would be wastefully consumed by acid, and more acid would be returned to the leaching process.

That reaction (1) occurs and could be a factor in the cementation reaction is illustrated by the corrosion behavior of iron in acid solution. The corrosion rate of low-carbon iron in $0.33N$-H_2SO_4 is constant and independent of the rate of movement of the acid relative to the metal in the absence of oxygen. Admission of oxygen to the system results in greater corrosion which increases with increasing rate of movement of acid relative to the metal surface. This is justifiably explained as polarization of the iron with hydrogen (in an activated state) in the absence of oxygen and depolarization of the iron surface by reaction of the sorbed hydrogen with oxygen (Uhlig, 1962).

If oxidizing ions, such as cupric ion, also depolarize hydrogen-sorbed iron surfaces as oxygen does, then measurements of the tendency of iron to corrode in acid solutions with and without the presence of cupric ion will permit identification of the depolarizing reaction. Corrosion tendencies of iron in acid solutions were measured by means of voltaic-cell experiments.

VOLTAIC CELL EXPERIMENTS

Small pieces of Armco ingot iron having a polished surface about half an inch square were used as anodes and a saturated calomel electrode as cathode in a voltaic cell contained in a three-neck glass bottle. The iron cathode was soldered to a copper wire. All the copper wire immersed in the solution, the soldered joint, and all but the polished face of the iron were covered with paraffin wax so that only the polished iron was in contact with the solution at the cathode. Figure 1 is a sketch of the cell. The sulfuric acid electrolyte was boiled and purged with bottled nitrogen before use to eliminate oxygen from the system. Cell voltages were measured with a Beckman Zeromatic pH machine that permitted voltage measurement at zero
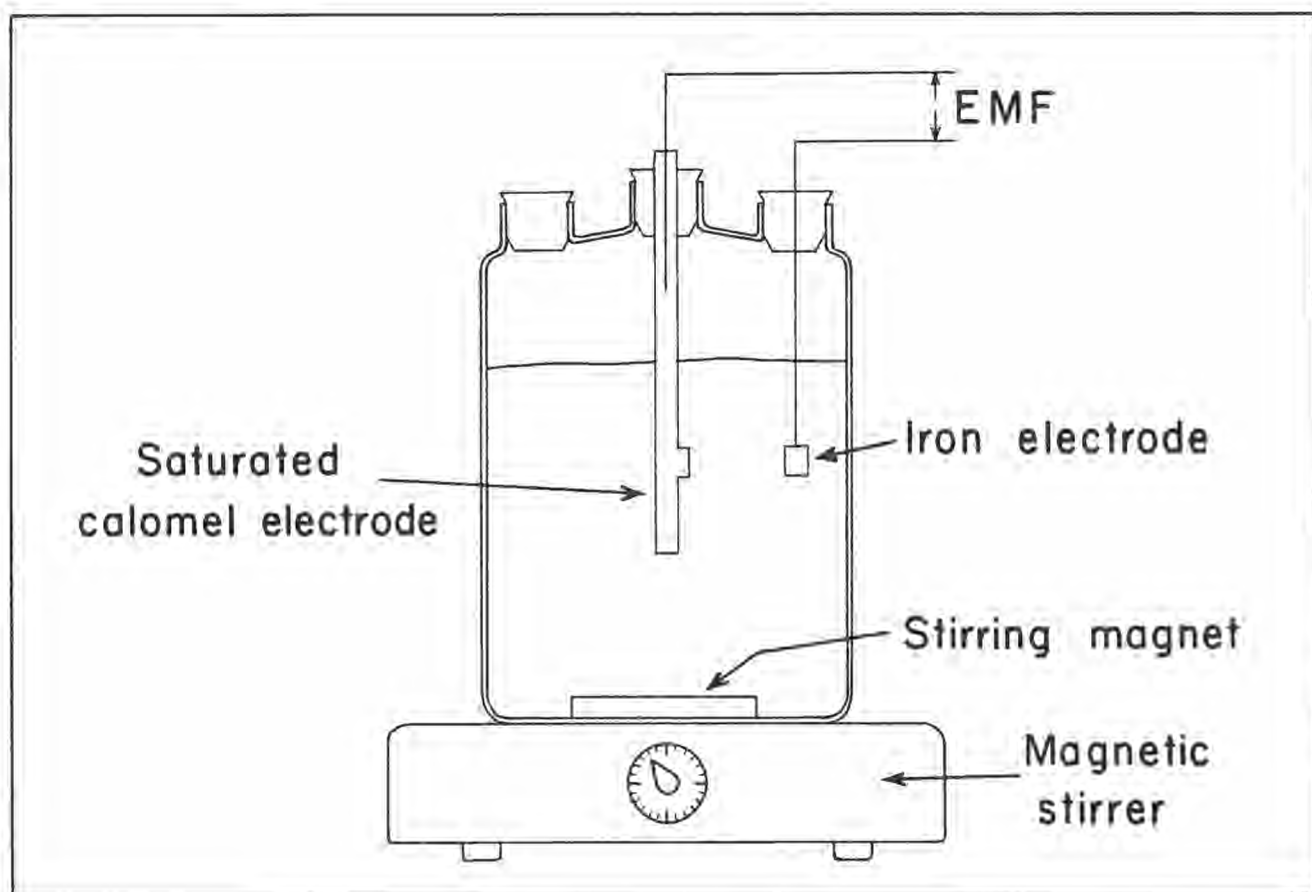
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Figure 1

SKETCH OF VOLTAIC CEL

current flow. Stirring was accomplished by means of laboratory magnetic stirrer. Voltages were measured for deoxygenated sulfuric acid solutions before am after additions of oxygen, cupric sulfate, and/or ferric sulfate. The solutions were stirred at stirring intensi ties of 0 to 10 on an arbitrary scale proportional to the speed of rotation of the stirring magnet. This ered the agitation range from stagnant solution ti vigorous agitation.

The steps in a single measurement were as follows:

1. Deoxygenated sulfuric acid solution added to cell which was being purged with nitrogen. The voltage slowly rose to a steady value; pH values were from 2 to 4.
2. Additions of $CuSO_4$ or $Fe_2(SO_4)_3$ to bring the solution to 1.0 gm of Cu^{++} or Fe^{+++} were made, or the solutions were saturated with oxygen.
3. The voltage, which changed upon addition of metal salts or oxygen, was recorded when it reached a steady value.
4. Voltage measurements were taken at zero, at medium, and at vigorous agitation rates (0, 4, and 10, respectively, on the arbitrary stirring scale), time being allowed for steady reading at each agitation rate.

5. Voltage readings were taken as the stirring was reduced stepwise to zero.

With the acid solutions (pH values from 1 to 4), the voltage at zero stirring rose slowly to a maximum value and then, as stirring was started, decreased slightly but remained relatively constant as stirring was made more intense. Addition of metal salt or saturation with oxygen reduced the voltage of the cell, the greatest decreases being observed with copper sulfate and with oxygen additions. The exact voltage and the extent of the voltage lowering varied from experiment to experiment, but lowering of the voltage was observed with each addition. Table 1 contains data for a typical experiment.

TABLE 1. EMF OF VOLTAIC CELL FOR H_2SO_4 AND FOR H_2SO_4 PLUS $CuSO_4$ (Typical Data)

STIRRING RATE	EMF (MV)				REMARKS
	H_2SO_4 ALONE		$H_2SO_4 + CuSO_4$		
0	625*	595**	622*	627**	Intial pH = 3.10
4	603	588	540	545	Final pH = 3.12
10	565	585	485	455	$CuSO_4$ conc. = 2.50 gm/L

* Increasing stirring rate.
** Decreasing stirring rate.

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700

H$_2$SO$_4$

H$_2$SO$_4$

600

H$_2$SO$_4$ + CuSO$_4$

EMF OF TEST CELL (MV)

H$_2$SO$_4$ + Fe$_2$(SO$_4$)$_3$

H$_2$SO$_4$ + Oxygen

H$_2$SO$_4$ + CuSO$_4$

H$_2$SO$_4$ + Fe$_2$(SO$_4$)$_3$

H$_2$SO$_4$

500

H$_2$SO$_4$ + Fe$_2$(SO$_4$)$_3$

H$_2$SO$_4$ + CuSO$_4$

○ – pH = 1 (approx)
△ – pH = 3 (approx)
X – pH = 4 (approx)

400

350

0   2   4   6   8   10
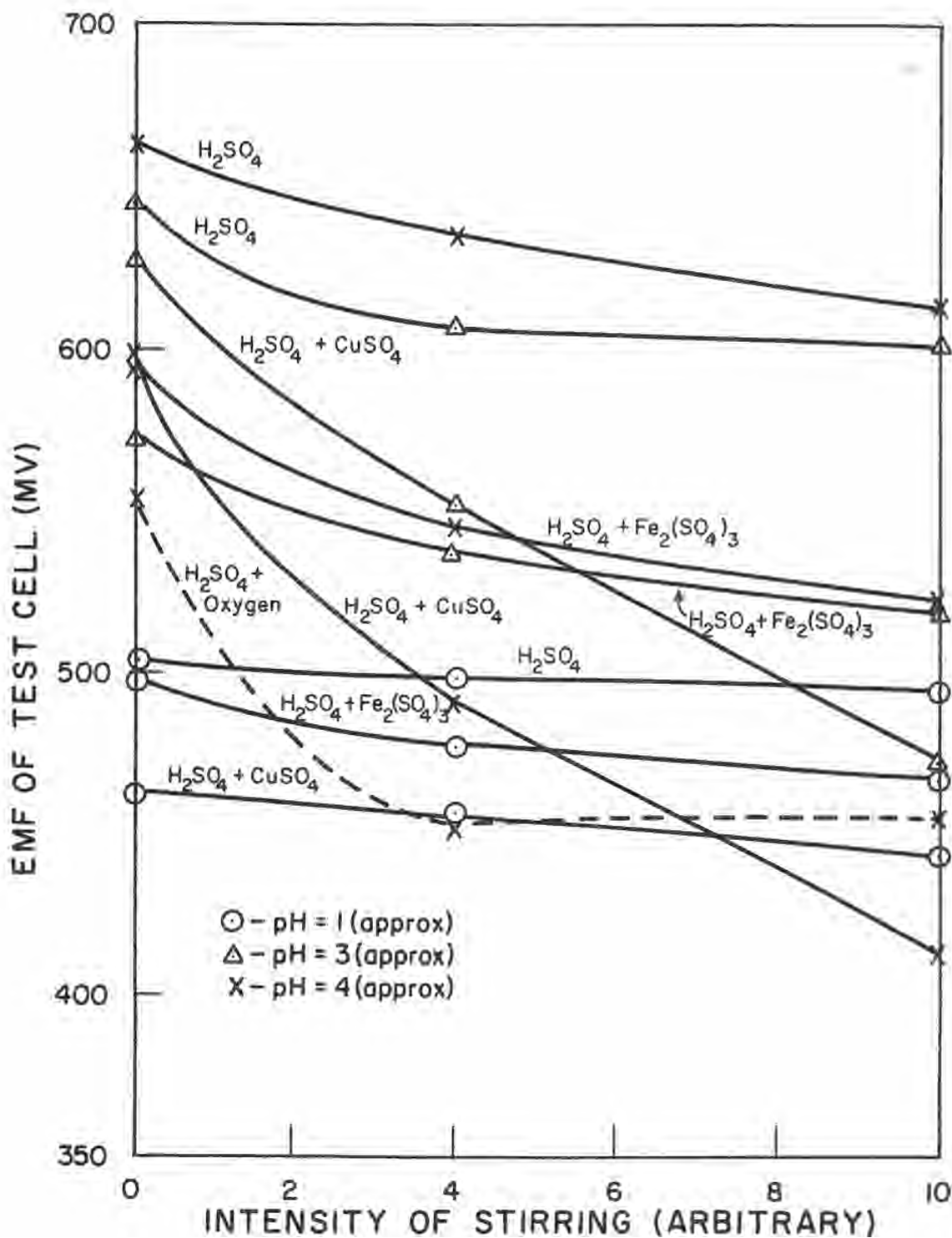INTENSITY OF STIRRING (ARBITRARY)

Figure 2
AVERAGE RESULTS OF SIXTY-TWO EXPERIMENTS

Figure 2 shows the average results of sixty-two experiments. Averaging the cell voltages for several similar experiments, which voltages are not very reproducible, has the effect of showing the average change in voltage, which is more reproducible. Inspection of Figure 2 reveals the extent of lowering of the cell voltages by oxygen, cupric ion, and ferric ion. The two upper curves show typical voltage behavior at different stirring rates for two deaerated acid solutions of different pH values. The dotted line shows the voltage behavior of a solution represented by the curve at the top after addition of oxygen. The zero stirring rate voltage has fallen considerably and increased stirring further reduces the voltage. This behavior is exactly what
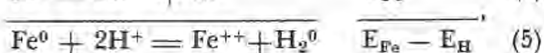
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would be expected from knowledge of the corrosion behavior of iron in acid solutions, with and without oxygen.

The curves for acid solutions containing copper sulfate and for acid solutions containing ferric sulfate show voltage reductions similar to those observed for oxygenated solutions. It appears that cupric ion and ferric ion have the same effect at the iron-solution interface that oxygen does: depolarization of the hydrogen-sorbed surface.

The exact voltage and the extent of lowering of the voltage by additions of oxygen, cupric sulfate, or ferric sulfate varied from experiment to experiment, though lowering of the cell voltage was always observed after additions were made. The lack of precision in voltage measurement is not surprising in this system. It is due to the variable condition of the surface of the iron electrode and the effect of surface conditions on hydrogen overvoltage on iron. It is well known that gas overvoltages at metal surfaces increase as the surface is made smooth and decrease as the surface is roughened (Uhlig).

DISCUSSION OF CELL VOLTAGES

When an iron electrode is immersed in sulfuric acid solution, the net result is the sum of two half reactions

$$2H^+ + 2e^- = H_2^0 \qquad -E_H \qquad (6)$$
$$Fe^0 = Fe^{++} + 2e^- \qquad E_{Fe} \qquad (7)$$
$$\overline{Fe^0 + 2H^+ = Fe^{++} + H_2^0 \qquad E_{Fe} - E_H} \qquad (5)$$

and the tendency for the reaction to go as written is measured by the sum of the electrode potentials for the half reactions. The more positive the sum of the voltages, the greater is the tendency of the corresponding reaction to go as written.

A half-reaction voltage may be written in terms of its standard EMF, E^0, and a function of the thermodynamic activities of the substances taking part in the reaction (Latimer, 1952); for example,

$$E_H = E_H^0 - \frac{RT \log a_{H^+}^2}{nF},$$

where R is the gas constant, T the absolute temperature, F the Faraday constant, n the number of electrochemical equivalents in the chemical equation, and a_{H^+} the thermodynamic activity of hydrogen ion in the solution. At 25°C, E_H becomes

$$E_H = E_H^0 - \frac{0.0591 \log a_H^2}{2}$$

and

$$E_{Fe}, \ E_{Fe} = E_F^0 - \frac{0.0591 \log a_{Fe^{++}}}{2},$$

Values of E° are to be found in tables (Latimer). E_H^0 is the standard reference EMF and is assigned the value *zero*.

At

$$p_{H_2} = 1 \text{ atm}, \ E_H = 0 - \frac{0.0591 \log a_H^2}{2} = 0.0591 \text{ pH}.$$

Also,

$$E_{Fe} = 0.414 - \frac{0.0591 \log a_{Fe^{++}}}{2}.$$

Then,

$$E_{Fe} - E_H = 0.414 - 0.0291 \log a_{Fe^{++}} - 0.0591 \text{ pH}. \qquad (8)$$

If reaction (5) were at equilibrium, $E_{Fe} - E_H$ would be zero and E_H would be equal to E_{Fe}. Equilibrium would require a value of $a_{Fe^{++}} = 10^{20}$ at pH = 3 and $p_{H_2} = 1$ atmosphere. It is apparent that equilibrium would not be possible at any imaginable condition for the reaction as written. However, a quasiequilibrium is possible if high enough hydrogen overvoltages occur. At the conditions of quasiequilibrium, E_H is made up of two parts, that due to a_H is 0.0591 pH at $p_{H_2} = 1$ atmosphere, and the overvoltage, E_i

Then, for the conditions of quasiequilibrium, equation (8) gives

$$E_H = E_{Fe} = E_{ov} + 0.0591 \text{ pH}$$
$$= 0.414 - 0.0296 \log a_{Fe^{++}}. \qquad (9)$$

For the experimental cell, the total voltage, E_T, is the sum of the voltages for the half reactions at the two electrodes. The cathode voltage is that of the standard saturated calomel electrode, C_c, and the anode voltage is either E_H or E_{Fe}, assuming quasiequilibrium. Selecting E_H,

$$2e^- + Hg_2Cl_2(s) = 2Cl^- + 2Hg^0$$
$$H_2^0 = 2H^+ + 2e^-$$
$$\overline{H_2^0 + Hg_2Cl_2(s) = 2Hg^0 + 2H^+ + 2Cl^-}$$
$$E_c = 0.2415$$
$$E_H$$
$$\overline{E_T = 0.2415 + E_H}$$

Substituting equation (9) for E_H,

$$E_T = 0.2415 + E_{ov} + 0.0591 \text{ pH} \qquad (10)$$

or

$$E_T = 0.2415 + 0.414 - 0.0296 \log a_{Fe^{++}}$$
$$= 0.656 - 0.0296 \log a_{Fe^{++}} \qquad (11)$$
$$> 0.656 \text{ in the range of } (Fe^{++}) \text{ for } a_{Fe^{++}} < 1 \qquad (12)$$
$$< 0.656 \text{ in the range of } (Fe^{++}) \text{ for } a_{Fe^{++}} > 1. \qquad (13)$$

In the experiments described here, the highest cell voltage obtained was 0.685 volt, which value was found by allowing sufficient time for the build-up of hydrogen overvoltage at the iron electrode. This was 5 to 10 minutes. The maximum hydrogen overvoltage on iron as reported in the literature is about 0.55 volt (Thompson, 1939) for conditions of zero current flow. Using the maximum observed voltage and a pH value of 3, which was the pH at the observed maximum voltage, equation (10) indicates that the maximum overvoltage encountered in these experiments was

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0.266 volt. Equations (10) and (12) together show that the cell voltage, under the conditions of zero or very small (Fe++) that existed in the solutions used, would have a maximum value greater than 0.656 volt, which agrees with the experimental observations very well. Further, the maximum hydrogen overvoltage observed is much less than the maximum reported in the literature and could be generated easily by the reaction of hydrogen ions with the iron electrode when the (Fe++) is low, as it was in the experimental cell. According to equation (9).

$$\log a_{Fe^{++}} = \frac{0.414 - E_{ov} - 0.0591 \text{ pH}}{0.0296}.$$

At pH = 3 and E_{ov} = 0.266,

$$\log a_{Fe^{++}} = \frac{0.414 - 0.266 - 0.0591 \times 3}{0.0296}$$

$$= -1.00$$

$$a_{Fe^{++}} = 0.1,$$

is a very reasonable value of (Fe^{++}) and is larger than $a_{Fe^{++}}$.

Thus, there is the chemical potential in the reaction between hydrogen ions and iron to generate a high hydrogen overvoltage on iron or to produce an activated hydrogen state of corresponding energy on the iron surface. The surface could be depolarized by oxidizing agents such as oxygen, cupric ion, or ferric ion, and the hydrogen activation energy dissipated, as was observed in the voltage measurements just described.

POSSIBLE APPLICATION OF RESULTS

If the hypothesis regarding reaction between cupric ion and activated hydrogen on the surface of iron is correct, and we do not have evidence that it is not, the possibility of conducting copper cementation with minimum wasteful reaction between iron and acid exists. Hydrodynamic conditions of maximum turbulence would maintain the greatest flux of copper ions through the fluid boundary layer at the iron surface. Reaction of the copper ions with activated hydrogen would produce hydrogen ions, as by equation (2), which in turn would decrease the concentration gradient for hydrogen ion in the boundary layer and slow down the diffusion of hyrdogen ions to the iron surface. The extent to which such control could be exerted is problematical because of mechanical and economic considerations. Work to determine the possible extent of optimizing the conditions for most economic cementation of copper from leach solutions is in progress.

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