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Young Ku[a]; Chi Hwa Chen[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, NATIONAL TAIWAN INSTITUTE OF TECHNOLOGY TAIPEI, TAIWAN, REPUBLIC OF CHINA

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Kinetic Study of Copper Deposition on Iron by Cementation Reaction

YOUNG KU* and CHI-HWA CHEN
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL TAIWAN INSTITUTE OF TECHNOLOGY
TAIPEI, TAIWAN 107, REPUBLIC OF CHINA

Abstract

Cementation of copper on iron powder was shown to be a feasible process to achieve a high degree of copper removal over a broad operational range. First-order kinetics were followed for both the copper concentration and the surface area of iron. To minimize the effect of copper-hydroxyl formation and excess iron consumption, the cementation process was found to be more practical in weak acidic conditions

Key Words: Copper removal; Cementation; Metal displacement

INTRODUCTION

The occurrence of heavy metals in an aquatic environment is known to cause severe pollution problems. Various treatment processes have been studied and developed to remove heavy metals from wastewaters (*1*). The cementation process has been considered to be an effective alternative for the removal of heavy metals from wastewaters. The process utilizes a less-toxic electropositive solid metal as a sacrificing reduction agent to recover the more-toxic electronegative dissolved metal species originally present in the wastewater. The advantages of the cementation process include its relatively simplicity, ease of control, and the possible recovery of valuable metals. However, the consumption of sacrificing metal and the redox potential of sacrificing metals limit the application of this process (*2*, *3*).

The removal of heavy metals by cementation has been studied by a number of researchers (*4–7*), but little work has been carried out on the kinetics of this process. In this particular study, the cementation process

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*To whom correspondence should be addressed.

was studied using iron powder to remove the copper(II) species from aqueous solution. The primary interests were in the effects of such operational factors as solution pH, reaction time, iron dosage effect on copper removal, the inhibition of the cementation reaction by metal-hydroxyl complex and hydrogen gas formation, and the establishment of cementation kinetics based on the deactivation model.

THEORETICAL CONSIDERATION

The cementation process can be described as a galvanic cell; for instance, the main chemical reaction involved in the cementation of copper species by iron is represented by the following redox reaction:

$$\mathrm{Fe} + \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Fe}^{2+} + \mathrm{Cu} \qquad (1)$$

During cementation, copper is deposited at cationic sites on the iron surface while dissolution of iron takes place at anionic sites. Even assuming that no other species is present in the aqueous solution, some redox side reactions relevant to the cementation of copper by iron are given below (*5–7*):

$$\mathrm{Fe} + 2\mathrm{H}^{+} \longrightarrow \mathrm{Fe}^{2+} + \mathrm{H}_2 \qquad (2)$$

$$2\mathrm{Fe} + 4\mathrm{H}^{+} + \mathrm{O}_2 \longrightarrow 2\mathrm{Fe}^{2+} + 2\mathrm{H}_2\mathrm{O} \qquad (3)$$

$$2\mathrm{Fe}^{3+} + \mathrm{Fe} \longrightarrow 3\mathrm{Fe}^{2+} \qquad (4)$$

$$2\mathrm{Fe}^{2+} + 2\mathrm{H}^{+} + \tfrac{1}{2}\mathrm{O}_2 \longrightarrow 2\mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O} \qquad (5)$$

$$\mathrm{Cu} + 2\mathrm{H}^{+} + \tfrac{1}{2}\mathrm{O}_2 \longrightarrow \mathrm{Cu}^{2+} + \mathrm{H}_2\mathrm{O} \qquad (6)$$

Stumm and Morgan (*8*) indicate that the ferrous ion (Fe^{2+}) is the predominant stable iron species present in aqueous solution in the absence of dissolved oxygen. To avoid the possible effect of dissolved oxygen, the experimental work of this research was carried out under a nitrogen atmosphere and the dissolved oxygen levels were kept under 0.5 mg/L. Thus, the competition of side reactions (3), (4), (5), and (6) do not have to be considered under our nitrogen-purged experimental conditions. At low pH levels, the only significant side reaction is assumed to be Reaction (2) between iron and the hydrogen ion.

Besides the redox reactions described above, complexation between the copper or iron species with hydroxyl ions (*9*, *10*) becomes important at high solution pH levels:

$$Cu^{2+} + nOH^- \longrightarrow Cu(OH)_n^{2-n}, \qquad n = 1, 2, \ldots \tag{7}$$

$$Fe^{2+} + mOH^- \longrightarrow Fe(OH)_m^{2-m}, \qquad m = 1, 2, \ldots \tag{8}$$

The formation of metal hydroxyl complexes is highly pH dependent and may interfere with the cementation process. For alkaline solutions, Reactions (7) and (8) are favored, which may lead to the formation of metal hydroxide precipitates.

The overall reaction scheme of the cementation process for the Cu^{2+}–Fe system can be summarized as shown in Fig. 1. Assuming the solution is ideal and that the effect of electrolyte on the above reactions

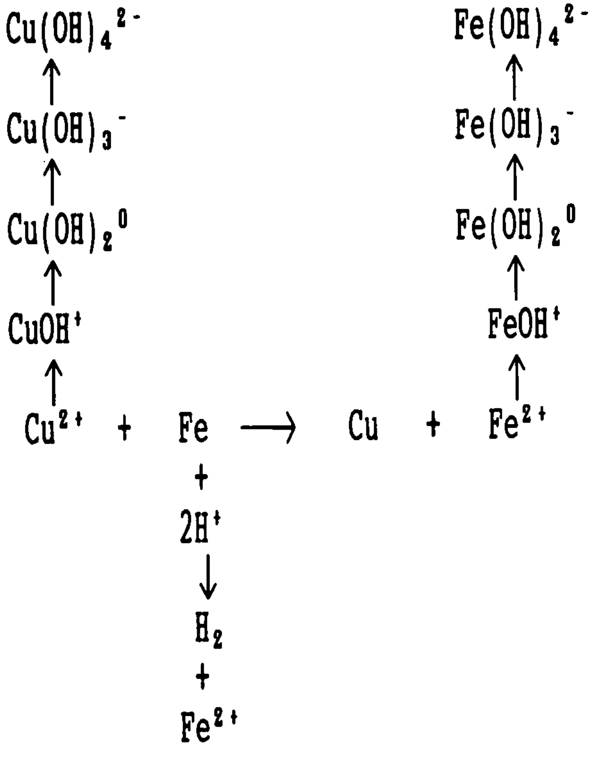


FIG. 1. The overall reaction scheme of the Cu^{2+}–Fe cementation system.

can be ignored, the initial metal species distribution in the solution can be determined with mass balances for various metal species and the appropriate equilibrium constants. The computed results are shown in Fig. 2 for copper species distribution as a function of solution pH conditions. The calculated species distribution based on coordination theory is shown to be strongly influenced by the solution pH.

Cementation can be considered to be essentially a solid–liquid reaction. The deposit of reduced metal, which nucleated at cathodic sites on the iron particle surface, gradually coalesce as cementation proceeds. Contact between the bulk solution and the residual iron core is lost after the surface sites of the sacrificing metal are totally occupied by the deposit of reduced metal, and thus the reaction ceases. The active site-losing behavior of the sacrificing metal is considered to be similar to the deactivation of a catalyst by coking. Assuming that cementation only occurs on the surface of sacrificing metal powders which are spherical and of uniform size, and ignoring

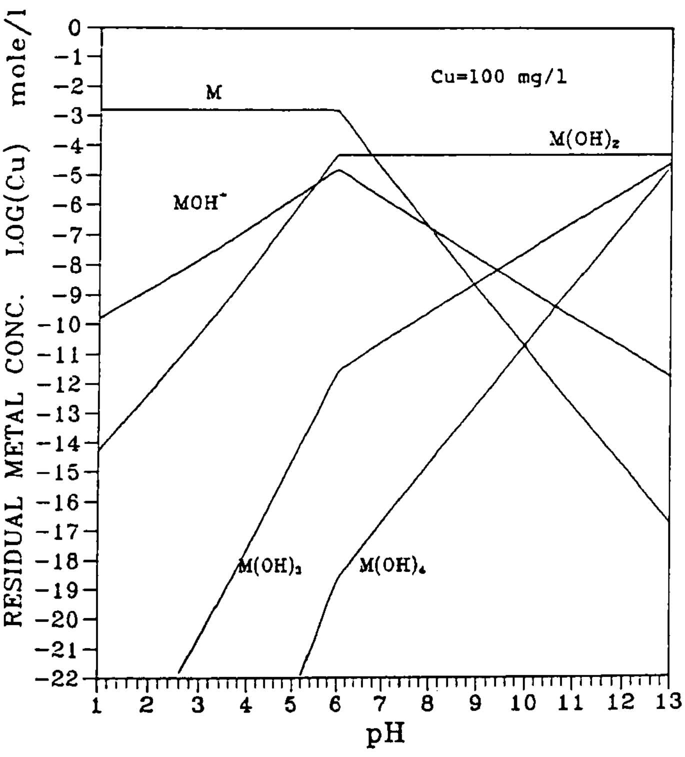


FIG. 2. Copper species distribution as a function of solution pH.

the codeposition of both sacrificing and reducing metals, the deactivation kinetic for the Cu^{2+}–Fe system can be described by

$$-d[\mathrm{Cu}]/dt = k[\mathrm{Cu}]^a[\mathrm{A/V}]^b \tag{9}$$

where [Cu] = concentration of copper ion
k = reaction rate constant
A = surface area of sacrificing iron metal
V = reactor volume
a, b = empirical constants

For iron particles of uniform size, Eq. (9) can be expressed with the amount of iron:

$$-d[\mathrm{Cu}]/dt = k'[\mathrm{Cu}]^a(m)^b \tag{10}$$

where m = amount of iron powder

Assuming only free copper species can deposit on the surface of the sacrificing iron metal, the concentration of free copper ion, $[Cu^{2+}]$, is

$$[\mathrm{Cu}^{2+}] = \frac{[\mathrm{Cu}]_t}{1 + \sum K_i(\mathrm{OH})_2}, \qquad i = 1, 2, \ldots \tag{11}$$

where $[Cu]_t$ = total copper concentration
K_i = equilibrium constants of complexing reactions between Cu^{2+} and OH^-

EXPERIMENTAL PROCEDURES

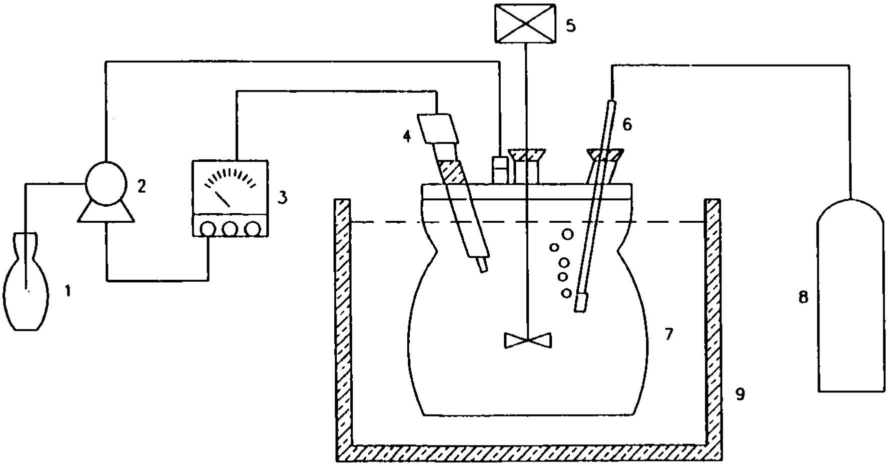
Iron powder of >99.99% purity with a medium size of 150 μm is used as the sacrificing metal. All experimental solutions were prepared with certified reagent grade chemicals and double distilled water.

Jar Tests

A series of cementation experiments was carried out for reaction equilibrium studies. Stock copper solutions were diluted to obtain the required initial copper concentrations. The dissolved oxygen levels of reaction solutions were measured and kept below 0.5 mg/L by nitrogen gas purging to minimize the effect of dissolved oxygen. A 100-mL sample solution was then transferred to a 250-mL flask. The pH of the sample solutions was adjusted with 1 *N* NaOH and 1 *N* H_2SO_4 solutions to preselected pH values. In this investigation the preselected pH values were from 2 to 9. Known amounts of iron powder were added to the flasks, and then the flasks were sealed with parafilm. The reaction solutions in the flasks were mixed by using an isothermal shaker bath. After mixing for 7 days, the cementation reaction of copper on iron was assumed to reach equilibrium, so the solution pH was monitored and recorded. The sample solution was then transferred and filtered immediately, using a 0.45 μm filter. The resulting filtrate was diluted if required and analyzed for its soluble metals content (copper and iron) by the atomic absorption method with a Varian Spectra AA-20 spectrophotometer. It should be mentioned that the method does not differentiate among various species of the same metal.

Batch Kinetic Experiments

The reaction kinetic studies were performed in a 2-L reaction vessel as shown in Fig. 3. The vessel was filled with copper solution of known concentration and then purged with nitrogen gas to keep the dissolved oxygen levels below 0.5 mg/L throughout the course of the reaction. Using an automatic pH controller, the solution pH was adjusted and maintained at the desired level by periodically adding acid or base to the solution.



1. NaOH Solution
2. Micro Tubing Pump
3. PH Controller
4. PH Electrode
5. Mixer
6. Gas Distributor
7. Reactor
8. N_2 Cylinder
9. Water Bath

FIG. 3. Schematic diagram of batch experimental unit.

Because several researchers (*2*, *4*) have indicated that cementation is a diffusion-controlled reaction at low mixing conditions, a mixing device with a Teflon mixer was used and the mixing speed was kept at 400 rpm after a series of tests was performed to eliminate the effect of mass transfer control on the reaction rate. A predetermined amount of iron powder was added to the copper feed solution. Appropriate temperature control was maintained for the reaction by containing the entire apparatus setup in a constant temperature water bath.

Typical reaction runs lasted 40 min to 1 h. At intermittent reaction time periods, a portion of the reactor solution was transferred and filtered using a 0.45-μm filter. The filtrate was analyzed for copper and iron concentrations by atomic absorption spectroscopy. Total sample volumes were kept below 3% of the total reactor solution volume. After the experiment was finished, the reaction solution was filtered for metal analysis, and the residual iron powder was rinsed with acetone, dried, and kept in a nitrogen environment prior to studying the surface morphology by scanning election microscopy (SEM) using a Cambridge S360 and the composition of the cemented deposits by x-ray diffraction (XRD) using a Philips MP 710.

RESULTS AND DISCUSSIONS

A series of jar tests was carried out to study the residual copper concentrations after cementation with iron for 7 days under various pH conditions at 25 ± 2°C. The experimental results shown in Table 1 indicate that the residual copper concentrations in solutions can be lowered substantially by using a sufficient amount of iron powder as a sacrificing metal. Throughout the solution pH range studied, the copper concentrations were reduced from about 100 mg/L to less than 0.6 mg/L. The residual concentrations of iron were found to be highly dependent on the initial solution pH levels, which, possibly due to side reactions, occurred as discussed previously, especially iron dissolution by hydrogen ion reduction. The addition of iron powder was found to cause significant changes in solution pH until an approximately constant value between 4.0 and 5.0 was obtained, despite the initial solution pH levels.

TABLE 1

Experimental Results for Jar Tests (initial copper concentration = 100 ± 1 mg/L; initial amount of iron powder = 50 ± 0.1 g/L; reaction time = 7.0 days)

Initial solution pH	2.0	3.0	4.0	5.0
Final copper concentration, mg/L	0.49	0.22	0.07	0.58
Final iron concentration, mg/L	410	97.5	61.7	88.2
Final solution pH	4.06	4.90	4.90	4.86

Batch reaction experiments were performed to study the global reaction kinetics of the reaction. It was discussed in the previous section that cementation may involve two or more parallel or series reactions, as shown in Fig. 1, with particular reactions dominating, thus setting the reaction order at different solution conditions. The effect of various amounts of iron powder on the cementation of copper ion at solution pH levels of 2, 3, and 4 are shown in Figs. 4, 5, and 6, respectively. In most cases the experimental results indicate more than 80% copper removal can be obtained within 20 min of reaction time. The apparent cementation rate of copper was found to be slightly lower at pH 2 than at pH 3 or 4, which

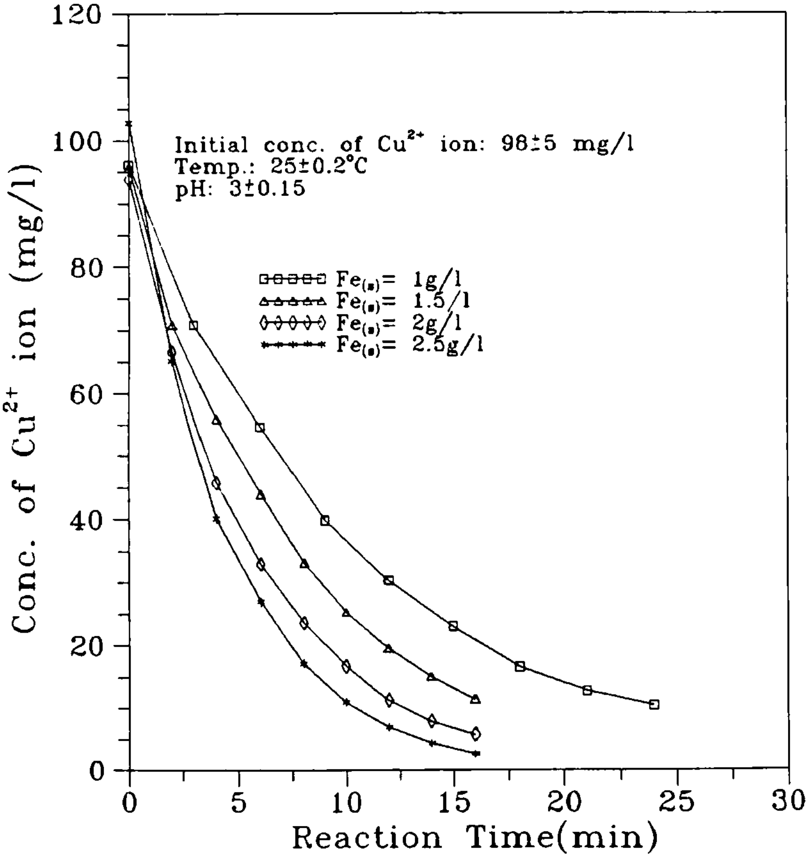


FIG. 4. The effect of the amount of iron powder on the cementation of copper ion on iron powder at solution pH 2.

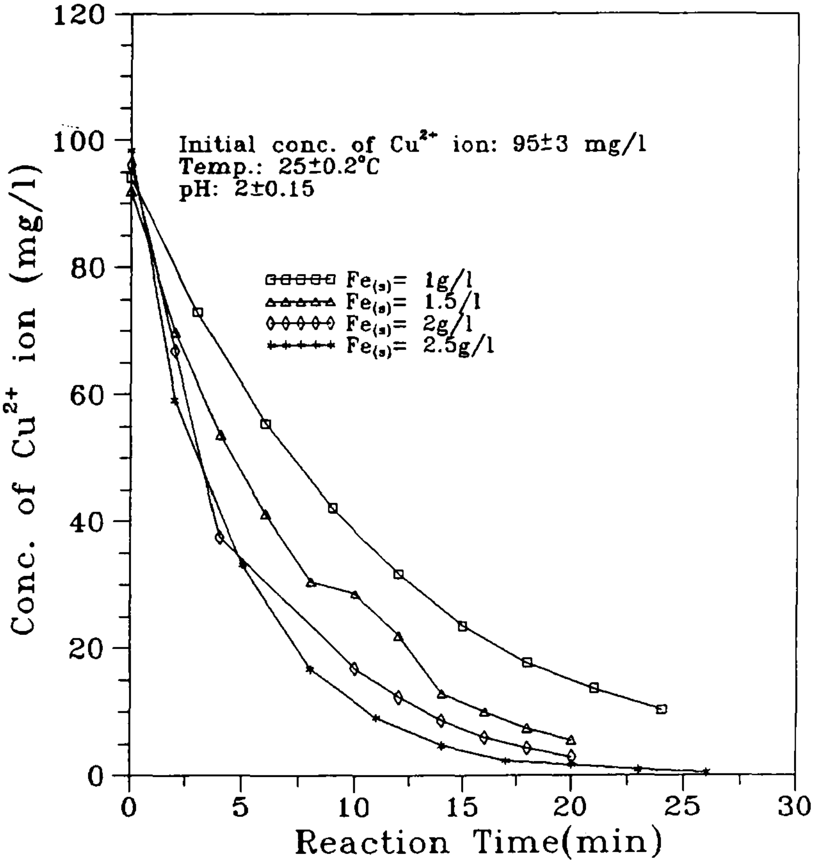


FIG. 5. The effect of the amount of iron powder on the cementation of copper ion on iron powder at solution pH 3.

may be explained by the fact that hydrogen ion reduction at very acidic conditions may lead to the evolution of hydrogen bubbles on the iron powder surface and inhibit the reduction of copper.

The calculated global reaction rates based on the experimental results gave very satisfactory correlations and were found to be approximately first order with both the total copper concentration and the amount of iron powder. Thus, the empirical constants of *a* and *b* in Eq. (9) are given a value of 1, and the global rate equation for copper removal becomes

$$d[\mathrm{Cu}]/dt = k_1[\mathrm{Cu}](m) \qquad (12)$$

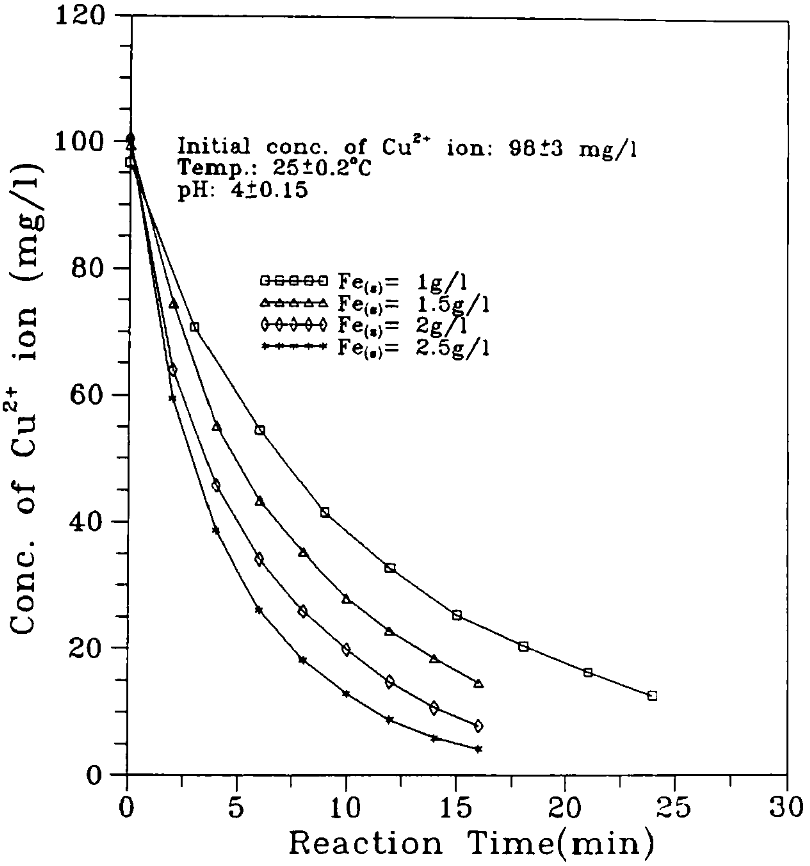


FIG. 6. The effect of the amount of iron powder on the cementation of copper ion on iron powder at solution pH 4.

The apparent reaction rate constants, k_1, obtained under various solution pH conditions are fairly constant, as shown in Table 2. The apparent kinetic parameters seem to support the assumption that only free copper ions can be adsorbed and reduced on the iron surface because almost all the copper species are present as Cu^{2+} free ion in the acidic solutions studied. But at neutral and basic solution pH conditions, the distribution of copper species may change significantly due to the formation of copper-hydroxyl complexes. Thus, the reaction rate is a strong function of solution pH.

The effect of solution temperature on the removal of copper ions by iron cementation was studied at 25, 35, 45, and 55°C. The experimental results are shown in Fig. 7. An elevated solution temperature slightly increases the cementation reaction rate. An Arrhenius plot (Fig. 8) based

TABLE 2
Kinetic Parameters Obtained by Regression for Copper Ion Cementation on Iron

Solution pH	k_1	a	b
2	0.047	1	0.85
3	0.046	1	0.95
4	0.041	1	0.92

on first-order kinetics indicated that the apparent activation energy for the Cu^{2+}–Fe cementation system is about 2.1 kcal/g·mol for the temperature range 25–55°C. The low activation energy values imply that solution diffusion is a possible rate-controlling step, because similar experimental results were observed by Agelidis et al. (2) for the Pb^{2+}–Fe system.

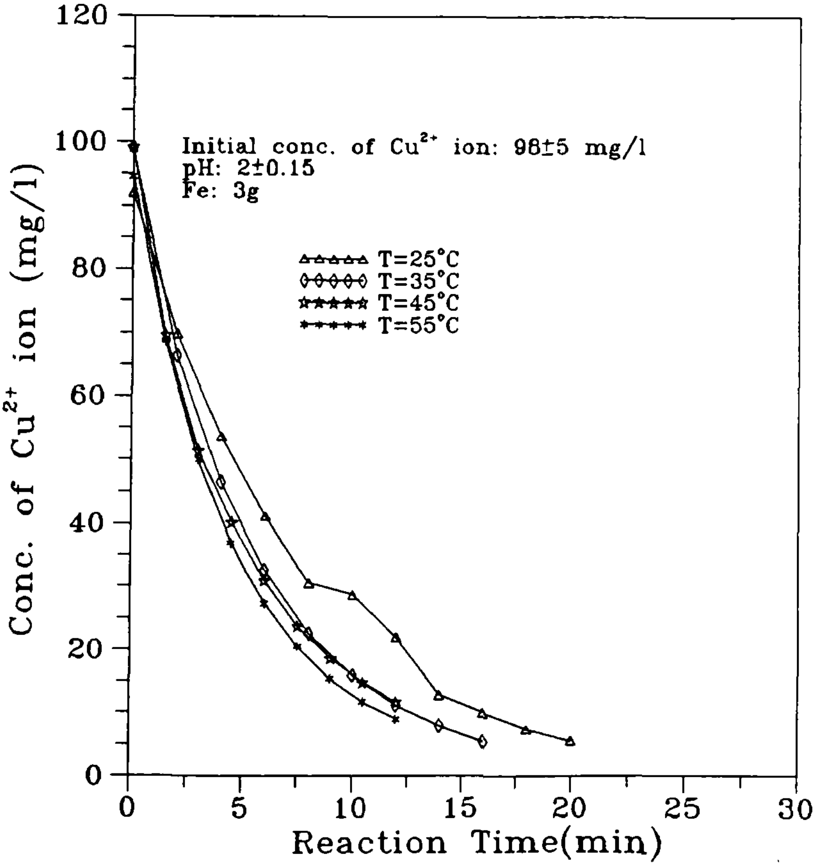


FIG. 7. The effect of solution temperature on the cementation of copper ion on iron powder.

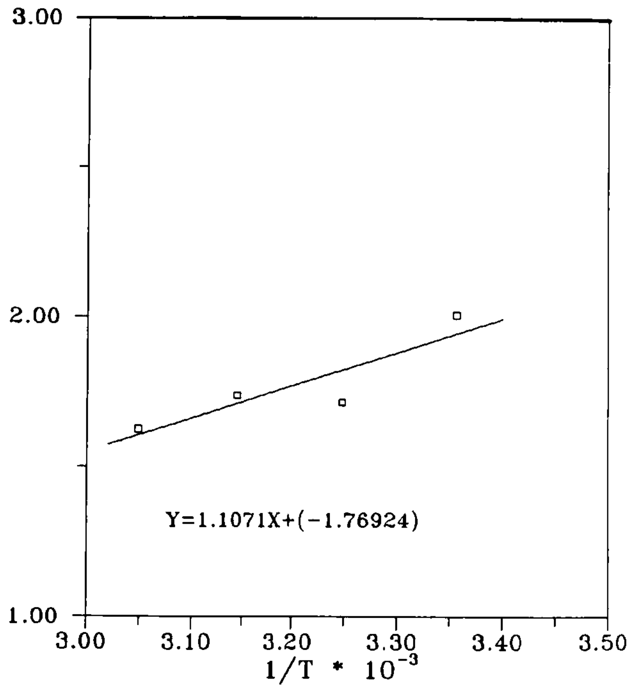


FIG. 8. The Arrhenius plot of the experimental results.

The consumption of iron powder under various conditions is presented in Figs. 9 and 10. Experimental results revealed that residual iron concentrations in solution are markedly greater than those that can be accounted for by copper cementation. These discrepancies were greater at lower solution pH levels and have been found by other researchers for different systems (*4*, *11*). The discrepancies of residual iron concentration, along with the observed gas evolution, confirm the assumption that the total consumption of iron, Fe_t, is caused mainly by the reduction of copper, Fe_{Cu}, and hydrogen ions, Fe_{H_2}:

$$Fe_t = Fe_{Cu} + Fe_{H_2} \tag{13}$$

Iron consumption of copper cementation was discussed previously with apparent first-order kinetics with an appropriate stoichiometry of Eq. (1):

$$Fe_{Cu} = \frac{56}{63.5}([Cu]_0 - [Cu]) = 0.88[Cu]_0(1 - e^{-k_t m t}) \tag{14}$$

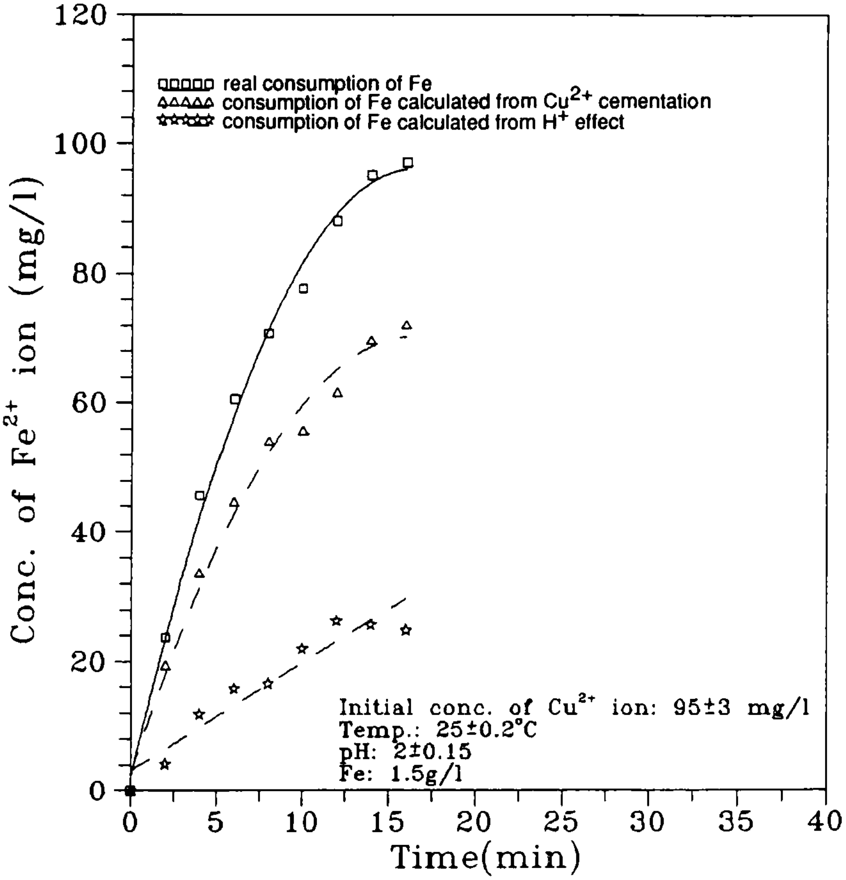


FIG. 9. The consumption of iron powder at solution pH 2.

where $[Cu]_0$ and [Cu] are total copper ion concentrations at the beginning of the reaction and at time *t*, respectively.

Excess iron consumption due to the reduction of hydrogen ion is calculated by subtracting the iron consumption due to copper cementation from the total iron consumption. It is assumed to be dependent on solution pH and the amount of iron powder. Figures 9 and 10 show that iron consumption caused by hydrogen reduction is linear, with the reaction time at constant pH conditions indicating a zero-order relationship to the amount of iron powder.

Even though the experimental results indicate that iron consumption by copper reduction is fairly independent of solution pH for acidic solutions,

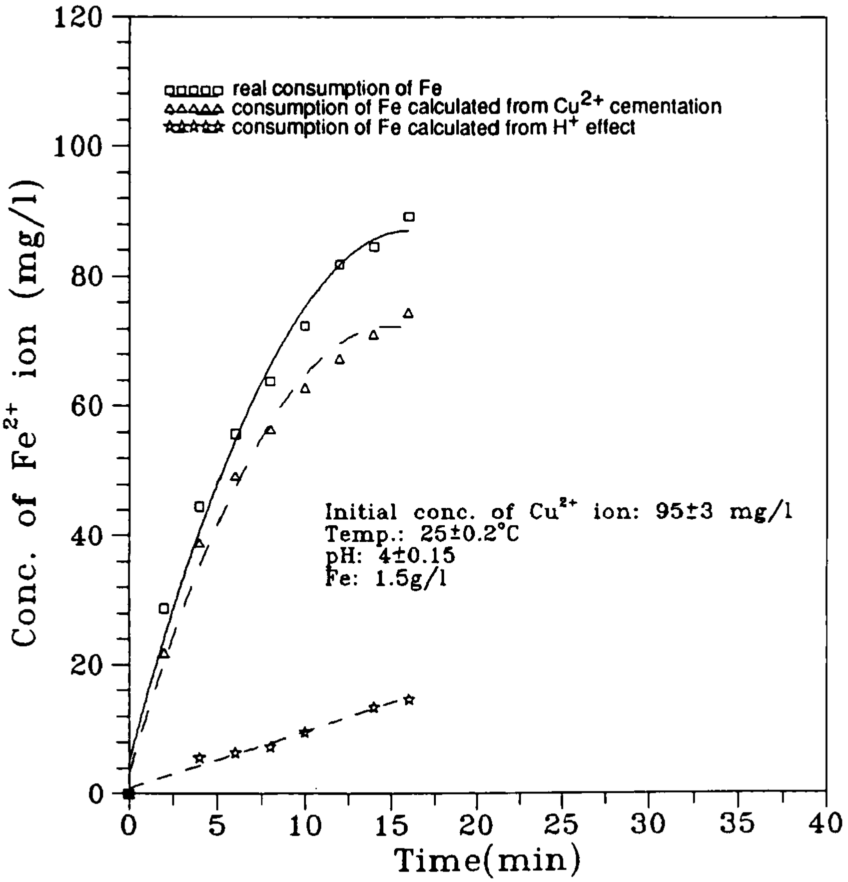


FIG. 10. The consumption of iron powder at solution pH 4.

iron consumption by hydrogen reduction was found to be highly pH dependent. The apparent reaction order for hydrogen ion concentration (H^+) was found to be about 0.15 by correlating the experimental results under various solution pH conditions. An empirical equation was derived as follows for the dissolution of iron by hydrogen reduction:

$$Fe_{H_2} = k_2'[H^+]^{0.15}t \tag{15}$$

where k_2' is the apparent rate constant of iron consumption by hydrogen reduction.

Combining Eqs. (13) and (14), the total iron consumption in solution at any reaction time t can be predicted by

$$\mathrm{Fe}_t = 0.88[\mathrm{Cu}]_0(1 - e^{-k_i m t}) + k_2'[\mathrm{H}^+]^{0.15}t \tag{16}$$

For a solution pH greater than 5, the second term of Eq. (16) would be minimal, and the iron consumption could be determined solely based on copper reduction. For more acidic solutions, the competition of hydrogen ions with copper ions for iron is evidently more important and makes the cementation process impractical.

XRD analysis was performed to study the composition of cemented deposits under various experimental conditions. The results indicate that copper deposits on an iron surface are almost all in the form of copper molecules. No indications of any Cu–Fe alloy or metal oxides/hydroxides were found on the surface. Examination of the cemented surfaces by using scanning-election microscopy (SEM) showed a sponge-like amorphous structure with irregular channels penetrate toward the iron core, as shown in Fig. 11. During the course of reaction, the iron surface acts as both cathode and anode. The nodular copper deposits indicate that copper cementation preferentially occurs at certain sites on the iron surface. The irregular channels observed are possibly etching pits caused by the dissolution of iron. The release of hydrogen gas bubbles from the surface may also decrease the uniformity of the deposited copper.

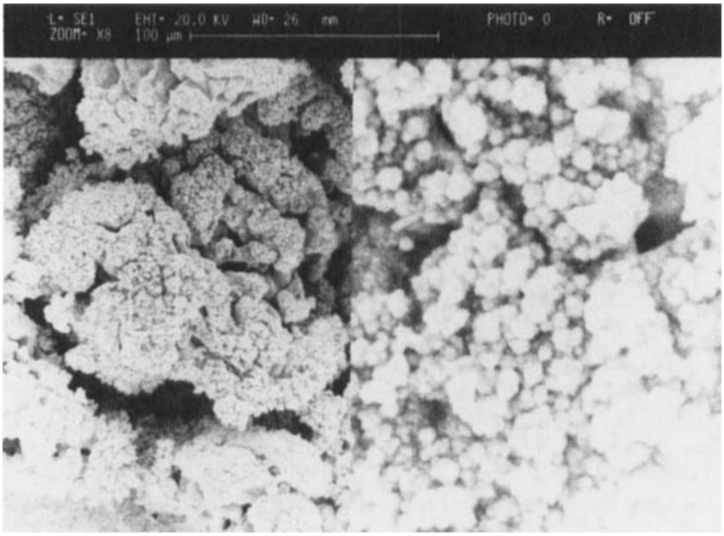


FIG. 11. SEM picture of the cemented iron surface.

SUMMARY

Based on this study of the cementation of copper on iron powder, the following conclusions were reached.

1. Cementation was shown to be a feasible process to achieve a high degree of removal of copper over a broad operational range.
2. Apparent reaction kinetics based on a deactivation model gives very satisfactory correlations for the experimental results. Both the copper concentration and the surface area of iron powder were first order to the cementation rate of copper.
3. The deposition rate of copper was found to be fairly independent of solution pH for acidic solutions, but the formation of copper hydroxyl complexes may interfere the copper deposition for neutral or alkaline solutions.
4. Excess iron consumption is caused mainly by the reduction of hydrogen ions, which is highly dependent on solution pH conditions. Empirical equations can be used to predict iron consumption by hydrogen reduction.
5. Considering the possible inhibition of the cementation rate at neutral and alkaline conditions, and the possible excess iron consumption at strong acidic conditions, the cementation process is most practically operated at weak acidic conditions of pH 4 to 5.
6. The resulting effluent containing dissolved iron may be recovered. It should not be discarded without proper treatment to avoid secondary pollution problems.

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