Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Gómez-Lahoz, C. , García-Herruzo, F. , Rodríguez-Maroto, J. M. and Rodríguez, J. J.(1992) 'Copper Removal from Water by Chemical Reduction with Sodium Borohydride', Separation Science and Technology, 27: 11, 1449 — 1468

To link to this Article: DOI: 10.1080/01496399208019436

URL: http://dx.doi.org/10.1080/01496399208019436

SEPARATION SCIENCE AND TECHNOLOGY, 27(11), pp. 1449–1468, 1992

Copper Removal from Water by Chemical Reduction with Sodium Borohydride

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Abstract

The use of $NaBH_4$ as a chemical reductant to precipitate copper from water has been studied. Initial Cu^{2+} concentrations of 25 and 40 mg/L have been checked, and complete removal can be achieved. When solid $NaBH_4$ is fed, BH_4^- to Cu^{2+} molar ratios higher than 2 were needed. This can be substantially improved by using $NaBH_4$ as a stabilized alkaline solution. A kinetic model is proposed which gives information about the relative rates of the two competitive reactions involved (Cu^{2+} and water reduction with BH_4^-) and allows the operating conditions leading to minimum BH_4^- consumption to be established.

INTRODUCTION

One of the recent increasing uses of sodium borohydride is for the removal of metals from plant effluents (*1–9*). Although this precipitation method is already being used in some industrial plants, there is still a lack of information about the chemistry and the kinetics of borohydride/metal systems in aqueous solution.

Removal of metal ions by chemical reduction to the metallic state could have, in principle, some advantages over conventional alkaline precipitation. Sludge may be easier to settle and dewater, and economic savings may be achieved in both capital costs and variable costs as a result of lower sedimentation areas and easier sludge handling and disposal procedures. Moreoever, when the leaching tests prove safety, the sludge may be declassified as hazardous and in some cases, especially for the most expensive metals (precious metals), they may be easily recovered. At the same time,

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some other advantages may be obtained from the use of chemical reduction precipitation, such as the destruction of some complexes (NH_3, CN^-, ...) which are frequent forms of copper(II) in wastewaters and which seriously hinder the use of alkaline precipitation.

Sodium borohydride shows properties that make it fairly interesting as a chemical reductant. One of the most important is that although it has a standard redox potential of −1.23 V, capable of reacting with water at any pH value with H_2 release, it can remain dissolved without reaction for large periods of time in strongly caustic solutions. It has a very low equivalent weight since eight electrons may be released:

$$BH_4^- + 3H_2O \rightarrow H_3BO_3 + 7H^+ + 8e^- \qquad (1)$$

The general equation for the reduction of divalent cations to the metallic state can be expressed by

$$BH_4^- + 4Me^{2+} + 3H_2O \rightarrow H_3BO_3 + 4Me^0 + 7H^+ \qquad (2)$$

Table 1 reports the removal weight ratios theoretically achievable for different metals.

Should other oxidant species be present, they may also be reduced by $NaBH_4$, and the amount of reagent needed to remove the heavy metals will be increased, with a sharp negative effect on the economy of the process. One of the most common oxidants is dissolved oxygen, which may react with both $NaBH_4$ and most of the reduced metallic species. Oxygen

TABLE 1
Theoretical Weight Ratios of Reduced Metal Obtainable from Ionic Species with Sodium Borohydride

Oxidation state	Weight ratio[a]
Cd^{2+}	12
Co^{2+}	6
Cu^{2+}	7
Ag^+	23
Pb^{2+}	22
Hg^{2+}	21
Hg^+	42
Ni^{2+}	6

[a] Weight ratio = maximum grams of metal reduced/gram of $NaBH_4$.

as well as almost every other oxidant species may be removed by pretreatment with less expensive reactants. Nevertheless, water will always be present and will undergo reduction with BH_4^- following reaction (3) to an extent depending mainly on the pH. Based on literature data (*10*, *11*), the kinetics of this reaction at pH values below 9 can be expressed by Eq. (4), where the preexponential factor units are $L \cdot mol^{-1} \cdot s^{-1}$.

$$BH_4^- + 3H_2O + H^+ \rightarrow H_3BO_3 + 4H_2 \qquad (3)$$

$$-d[BH_4^-]/dt = 6.62 \times 10^{12} e^{-4680/T}[H^+][BH_4^-] \qquad (4)$$

The main interest of this work is the stoichiometry and kinetics of the aqueous Cu^{2+}/BH_4^- system in conditions where no copper precipitation as hydroxide takes place, allowing the redox process itself to be analyzed.

EXPERIMENTAL

Simulated wastewaters were prepared by using deionized water with conductivity values ≤5 μmhos/cm. The necessary amount of a previously prepared solution of $CuCl_2 \cdot H_2O$ containing 1000 mg Cu^{2+}/L was added to obtain the desired initial concentrations of copper(II). Dilute HCl or NaOH was added to fix the initial pH in each experiment.

Merck (powder, for synthesis) sodium borohydride was used. Since sodium borohydride is highly hygroscopic, it was kept in a desiccator. Amounts of approximately 10 g were taken for experiments that were performed with solid borohydride. These were placed in a second desiccator, from which the necessary amount for each experiment was weighed. Stabilized water solutions of sodium borohydride were prepared with different concentrations of NaOH, and they were maintained at temperatures below 10°C. Immediately before each experiment the reducing capacity of the borohydride solution was measured by the Lyttle method (*12*). This analysis was also used for solid borohydride. Borohydride with a reducing capacity ≥97.5% the theoretical was always used.

The experimental runs were carried out in a 2.35-L cylindrical round-bottomed glass reactor provided with a glass anchor-like stirrer. Redox potential and pH were continuously registered by means of Cryson probes and pH meters, connected to a 2-channel register. All the redox values reported in the following sections are referred to the Ag/AgCl/KCl (3 *M*) electrode and expressed as oxidant potentials. Dissolved oxygen was measured by means of a Hanna Instruments, HI8543 oxymeter. The reactor was immersed in a thermostatic water bath where temperature was controlled within ±0.1°C by means of a Tectron apparatus. Stirring velocity was set at 450 rpm after previous experiments. Higher stirring velocities were found to produce instabilities in the pH probe.

Samples were taken by means of a Manostat three-way valve syringe, or a peristaltic pump, connected to a Millipore filtration system, with membranes "GSWPO2500" of 0.22 μm pore size. This sytem was chosen after previous experiments with cellulosic filters, where Cu^{2+} adsorption was observed, and with fritted-glass filters of 10–20 μm pore width, which showed filtering rates substantially lower than those needed to obtain the desired 10 to 20 samples per minute. Copper analyses were performed by AA using a Varian AA-475 instrument. XRD analyses were carried out on the precipitates by means of a Siemens D-501 apparatus.

RESULTS AND DISCUSSION

Figure 1 shows the Pourbaix diagram for copper at 25 and 10 mg/L concentrations. According to it, Cu^{2+} can be reduced either to metallic copper or to Cu_2O depending on the *E* and pH values. At pH above 4,

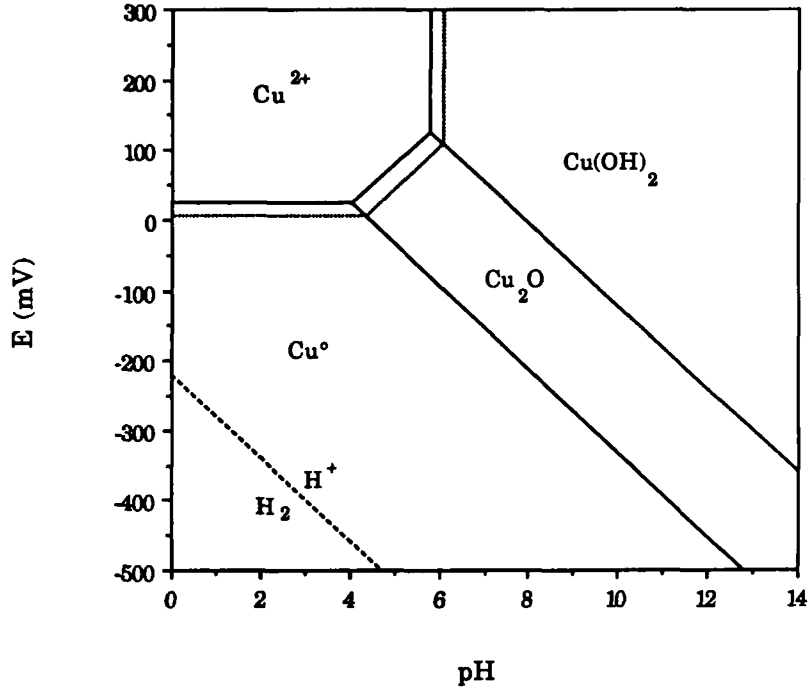


FIG. 1. Pourbaix diagram for copper: $[Cu^{2+}]$ of 40 (——) and 10 (···) mg/L. Oxidation potentials referred to the Ag/AgCl/KCl (3 *M*) electrode.

substantially higher reductant potentials are required to achieve a metallic copper precipitate. The diagram shows also the line corresponding to the equilibrium between H^+ and H_2, indicating that no reoxidation of the reduced copper species may be caused by water.

Copper(II) reduction to the metallic state, Eq. (5), follows the general Eq. (2), whereas the reduction to Cu_2O is given by Eq. (6). Water reduction by $NaBH_4$ may also occur according to Eq. (3).

$$BH_4^- + 4Cu^{2+} + 3H_2O \rightarrow 4Cu^0 + H_3BO_3 + 7H^+ \qquad (5)$$

$$BH_4^- + 8Cu^{2+} + 7H_2O \rightarrow 4Cu_2O + H_3BO_3 + 15H^+ \qquad (6)$$

In the presence of oxygen some other reactions should be considered, the most important being reoxidation of the reduced species of copper, Eqs. (7) and (8), as well as borohydride oxidation, given by Eq. (9).

$$Cu_2O + \tfrac{1}{2}O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O \qquad (7)$$

$$Cu^0 + \tfrac{1}{2}O_2 + 2H^+ \rightarrow Cu^{2+} + H_2O \qquad (8)$$

$$BH_4^- + 2O_2 + H^+ \rightarrow H_3BO_3 + H_2O \qquad (9)$$

Figure 2 shows the Cu^{2+} concentration, pH, and redox potential versus time obtained from a run performed in an oxygen-free stoppered reactor at an initial Cu^{2+} concentration of 25 mg/L using a $NaBH_4$ addition corresponding to a 25% excess of borohydride over the stoichiometric BH_4^-/Cu^{2+} ratio given by Eq. (5). As can be seen, in a period of time less than 20 s the pH decreases from 6 to about 4, whereas the redox potential curve exhibits a sharp initial negative slope, reaches a minimum, and then rises and stabilizes at a value above 50 mV, indicating that BH_4^- has been exhausted. The thermodynamic coordinates on the Pourbaix diagram are close to the zone of coexistence of the three species Cu^{2+}, Cu_2O, and Cu^0. The final concentration of Cu^{2+} shows that, although excess $NaBH_4$ was used, the amount of copper(II) removed was very low. Since no oxidants are present except copper(II) and water, reduction of water must have occurred even though the registered pH and redox potential values do not reach those corresponding to the H^+/H_2 equilibrium in the Pourbaix diagram. At acidic pHs, Reaction (3) occurs at a very high rate which, according to Eq. (4), leads to a half-reaction period of less than 0.01 s at pH 4. Most probably, BH_4^- is consumed locally at the addition point in a very short time and thus, although the thermodynamic region of occurrence of this reaction had been reached, the corresponding pH and E values could

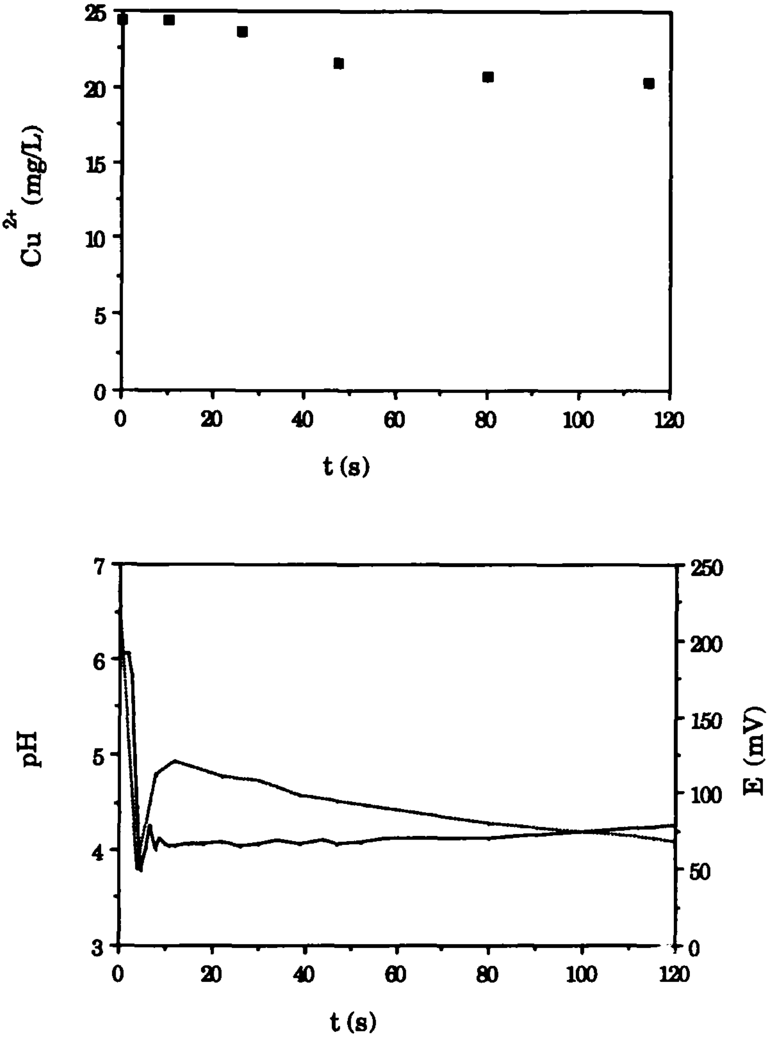


FIG. 2. $[Cu^{2+}]$, pH (——), and redox potential (···) evolution in oxygen-free reactor at 20°C and 450 rpm; pH_0 = 6.0; $[Cu^{2+}]_0$ = 385 μmol/L; $[NaBH_4]_0$ = 120 μmol/L.

have been not registered by the probes. Cu^{2+} reduction by BH_4^- must take place at least at a similar kinetic rate since the pH evolves toward acidic values.

The existence of mass-transfer limitations was confirmed by adding solid $NaBH_4$ to the reactor containing 1% NaOH aqueous solution in which borohydride is chemically stable. The time to reach a constant borohydride concentration at the sampling point was always found to be close to 20 s. Also, we performed a set of runs similar to the one described in Fig. 2 but with a change in the height at which borohydride was fed to the reactor, thus varying the relative positions of the probes. The pH and *E* versus time curves showed different shapes within the initial 20 s and finally stabilized at the values reported in Fig. 2. Thus, the time period needed for homogeneous mixing in the reactor is substantially higher than that required for chemical reaction.

Several experiments using different BH_4^- doses were carried out at the operating conditions described for Fig. 2. It can be concluded, in principle, that to achieve complete Cu^{2+} removal, BH_4^-/Cu^{2+} molar ratios somewhat higher than 2 are needed; a ratio of 2 yields 8 times more borohydride than that given by Eq. (5). At this rate the final *E* value is close to −800 mV, which leads to the conclusion that the precipitate corresponds to metallic copper. This was further confirmed by x-ray diffraction. This high BH_4^- excess can be attributed to the occurrence of water reduction (Reaction 3) to an undesirable extent. To diminish the contribution of this reaction and improve the mixing of the borohydride fed, we carried out a set of experiments using aqueous solutions of $NaBH_4$.

Figures 3 and 4 show the results obtained from two experiments performed at similar operating conditions using $NaBH_4$ as a solid and as an alkaline solution, respectively. In both cases the reactant fed was partitioned into several additions. The advantages of using alkaline $NaBH_4$ solution can be clearly noted from the Cu^{2+} concentration curves which reveal a substantially higher efficiency of borohydride (ϵ = mole of Cu^{2+} removed per mole of $NaBH_4$ added) in this second case ($\epsilon = 2.01$ versus 0.84 in the first addition). Moreover, the pH curves show different trends. The pH values at the initial period indicate that substantial inhibition of undesirable water reduction (Reaction 3) takes place when using alkaline $NaBH_4$ solution. Further additions give rise to initial pH peaks showing higher values in the case of alkaline solution, which confirms a larger inhibition of the water reduction reaction within the mixing period. With regard to the experimental procedure, it should be pointed out that working with alkaline $NaBH_4$ solution allows better reproducibility of results. We previously confirmed that the final results were not dependent on the number of additions of borohydride but only on the total amount fed.

Figures 5 and 6 report the results obtained from two experiments in fairly similar operating conditions using alkaline $NaBH_4$ at two different NaOH concentrations. As can be seen, NaOH concentration plays a very important role compared to what can be attributed to mixing improvement. The curves in Fig. 6 show a trend comparable to those observed when solid borohydride is used except that somewhat narrower peaks are now obtained after each addition as a result of mixing improvement.

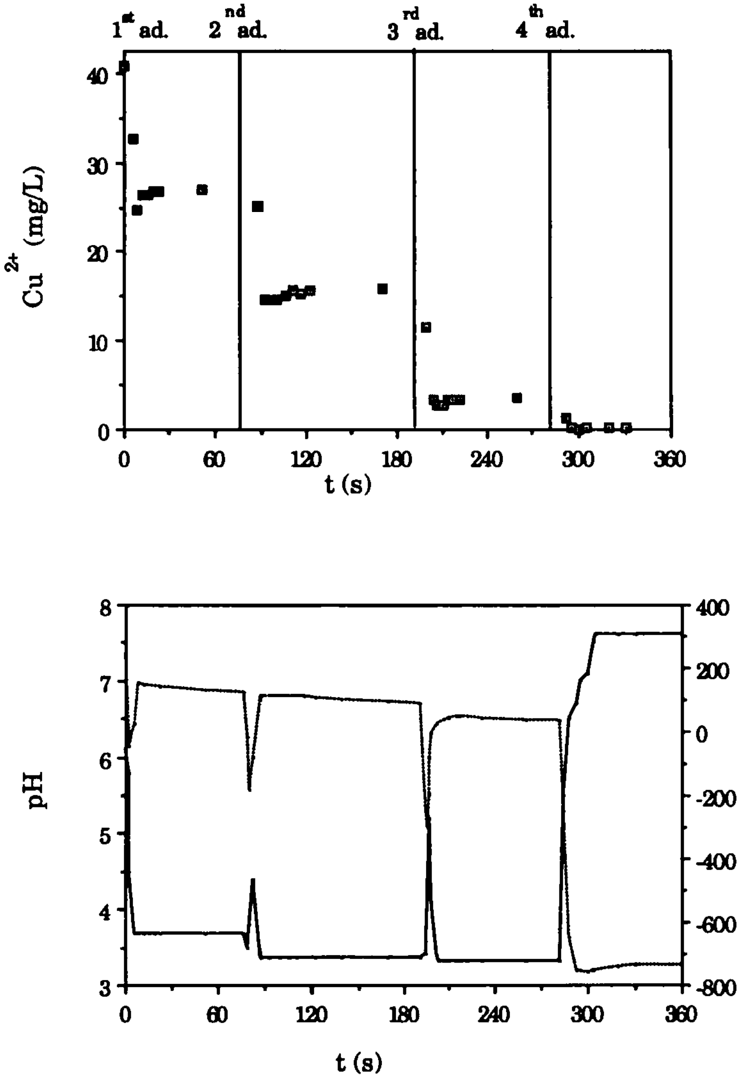


FIG. 3. [Cu^{2+}], pH (——), and redox potential (···) evolution in oxygen-free reactor at 20°C and 450 rpm for four additions of solid $NaBH_4$; pH_0 = 6.0; $[Cu^{2+}]_0$ = 640 μmol/L; $[NaBH_4]_0$ = 265, 285, 310, and 460 μmol/L.

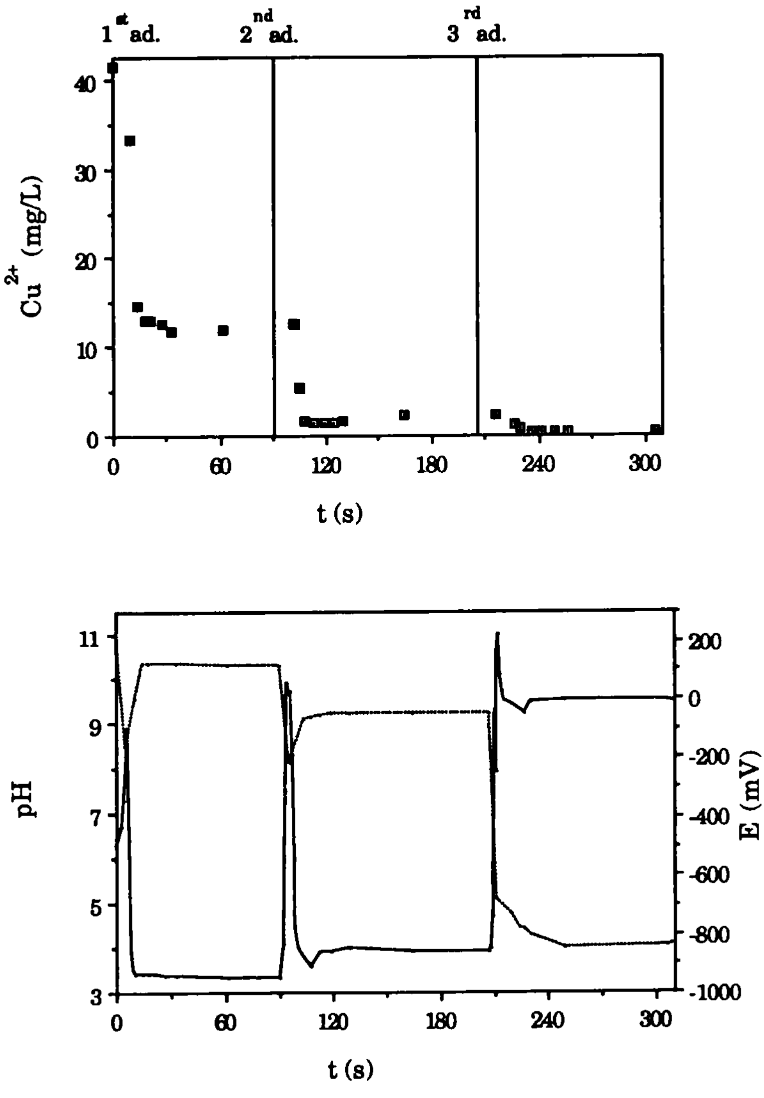


FIG. 4. [Cu^{2+}], pH (——), and redox potential (···) evolution in oxygen-free reactor at 20°C and 450 rpm for three additions of 230 μmol/L NaBH$_4$ and 425 μmol/L NaOH each as stabilized aqueous solutions; pH$_0$ = 6.0; [Cu^{2+}]$_0$ = 640 μmol/L.

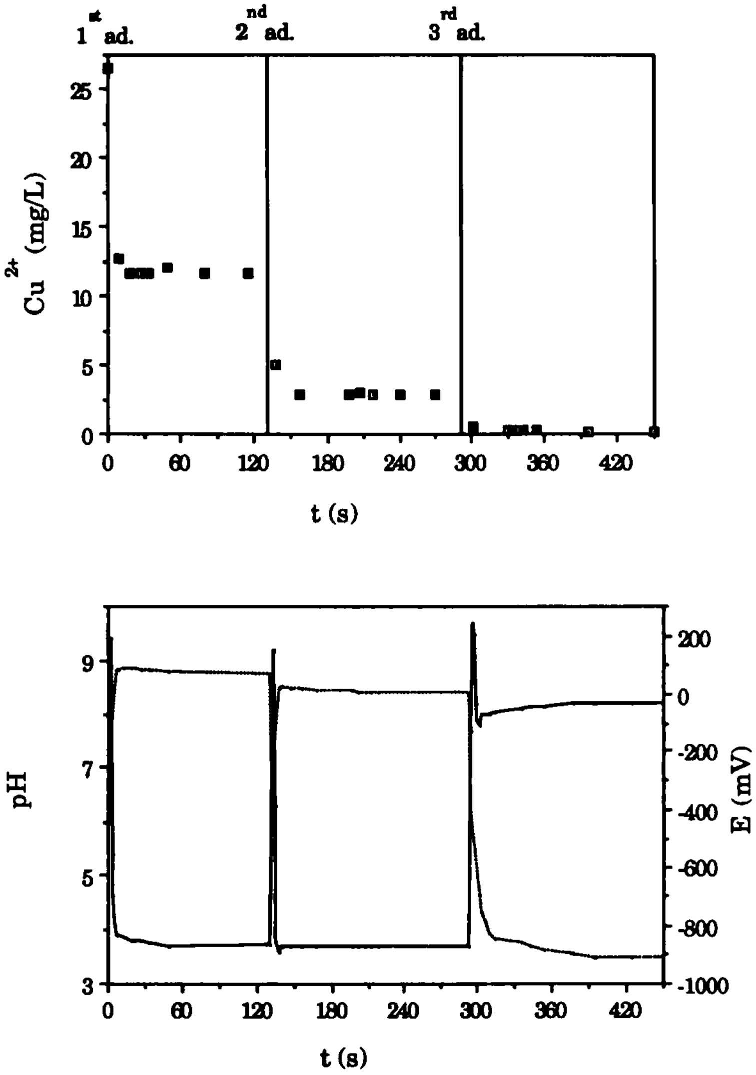


FIG. 5. $[Cu^{2+}]$, pH (——), and redox potential (···) evolution in oxygen-free reactor at 20°C and 450 rpm for three additions of 100 μmol/L $NaBH_4$ and 215 μmol/L NaOH each as stabilized water solutions; $pH_0 = 6.0$; $[Cu^{2+}]_0 = 415$ μmol/L.

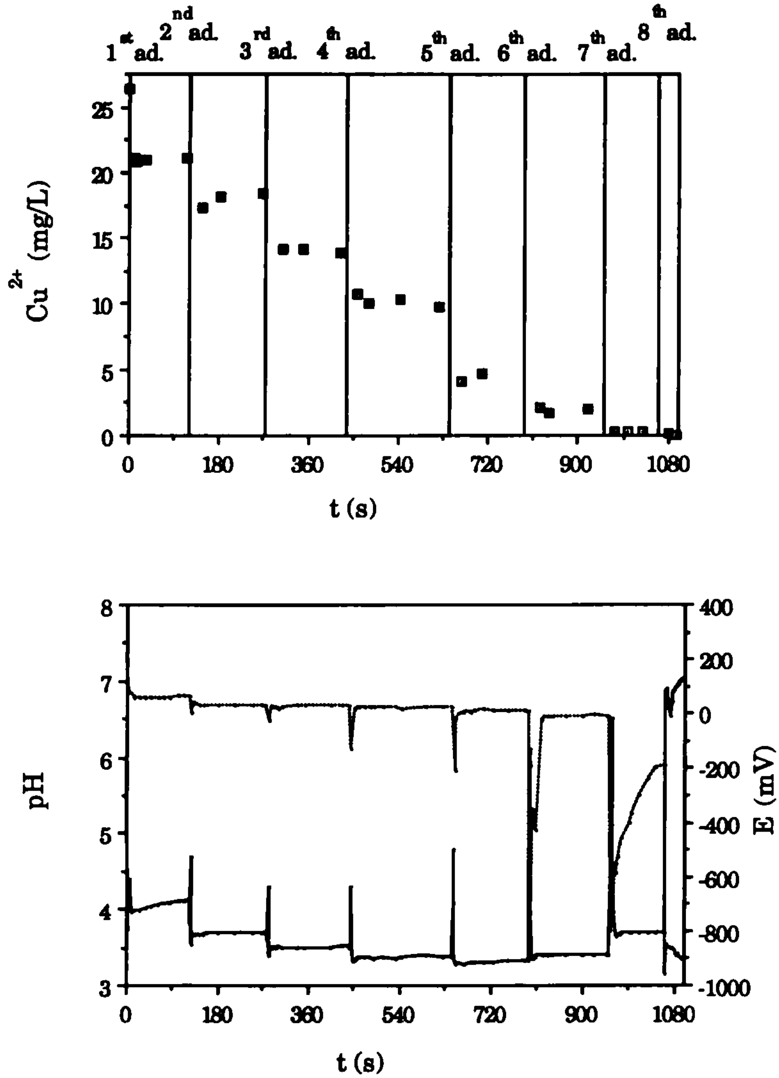


FIG. 6. [Cu^{2+}], pH (——), and redox potential (···) evolution in oxygen-free reactor at 20°C and 450 rpm for eight additions of 100 μmol/L NaBH$_4$ and 0.2 μmol/L NaOH each as stabilized water solutions; pH$_0$ = 6.0; [Cu^{2+}]$_0$ = 415 μmol/L.

Initial pH showed no significant effect within the mildly acidic values investigated in this work, as can be seen from Figs. 5 and 7. In fact, when one starts at pH 5, the expected additional BH_4^- consumption needed to reach pH 6 should be no more than 10 μmol/L.

To check the effect of temperature within a range of practical interest, we carried out an experiment under conditions similar to those used in the run shown in Fig. 5. The results, reported in Fig. 8, show no significant influence of this variable within the range investigated, probably due to the aforementioned mass-transfer control of the rate of the process.

Increasing initial Cu^{2+} concentration to ~40 mg/L showed little effect on borohydride efficiency, as can be seen from Figs. 5 and 9. The resulting values for the first addition are $\epsilon = 2.14$ and 2.26, respectively. The corresponding pH and E values are fairly close.

The presence of dissolved oxygen should be an important factor affecting borohydride efficiency in Cu^{2+} removal (Eqs. 7–9). The possible contribution of Reaction (9) was checked from experiments carried out in a stoppered reactor loaded with oxygen-saturated distilled water. After borohydride was fed, no significant consumption of dissolved oxygen was observed within the 30-min period investigated, which allows Reaction (9) to be neglected unless the presence of copper has some catalytic effect on that reaction.

Figure 10 presents the results obtained when working with an unstoppered reactor. The remaining experimental conditions are similar to those described for the runs shown in Fig. 5. As can be seen from the dissolved oxygen and redox potential curves, significant reoxidation takes place, although it does not affect the final concentration of Cu^{2+}, which is completely removed from solution at the BH_4^- dose used in the experiment. Thus, reoxidation must give rise to the formation of Cu_2O and $Cu(OH)_2$ from metallic copper, as expected from the final pH value.

Model Proposal

From the experimental results obtained, we conclude that copper(II) reduction with BH_4^- proceeds faster than does the borohydride/water reaction at pH values higher than 5, as confirmed from the evolution of the system to acidic pHs. Nevertheless, H^+ production will increase the rate of the water reduction reaction. When no external action is exerted on the pH of the medium, it seems reasonable to assume an overall stoichiometry where neither consumption nor production of H^+ takes place. With this hypothesis, Reactions (5) and (3) give rise to

$$2BH_4^- + Cu^{2+} + 6H_2O \rightarrow 2H_3BO_3 + 7H_2 + Cu^0 \qquad (10)$$

for copper(II) reduction to the metallic state.

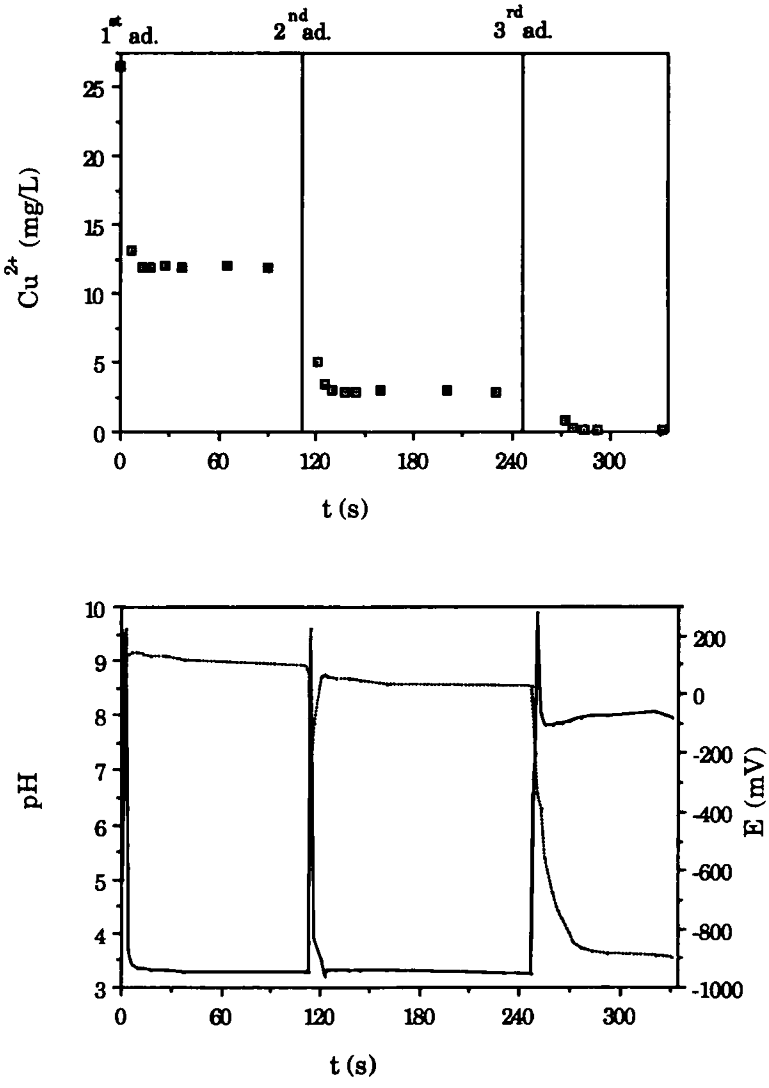


FIG. 7. [Cu^{2+}], pH (——), and redox potential (···) evolution in oxygen-free reactor at 20°C and 450 rpm for three additions of 110 μmol/L $NaBH_4$ and 215 μmol/L NaOH each as stabilized water solutions; pH_0 = 5.0; [Cu^{2+}]$_0$ = 415 μmol/L.

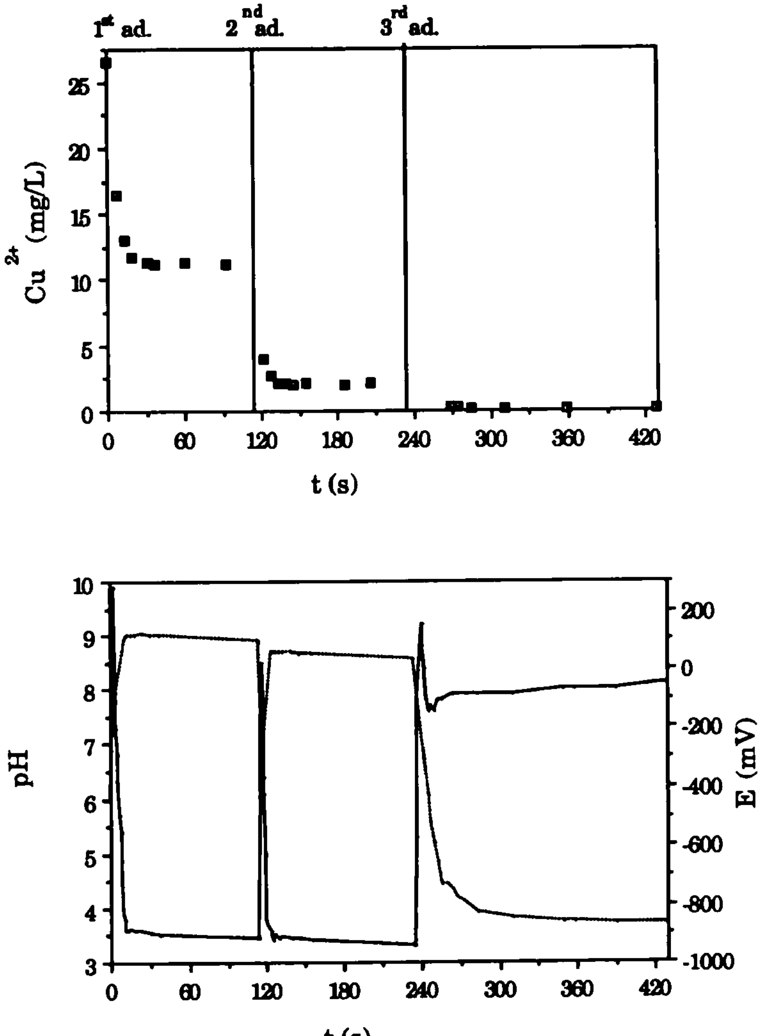
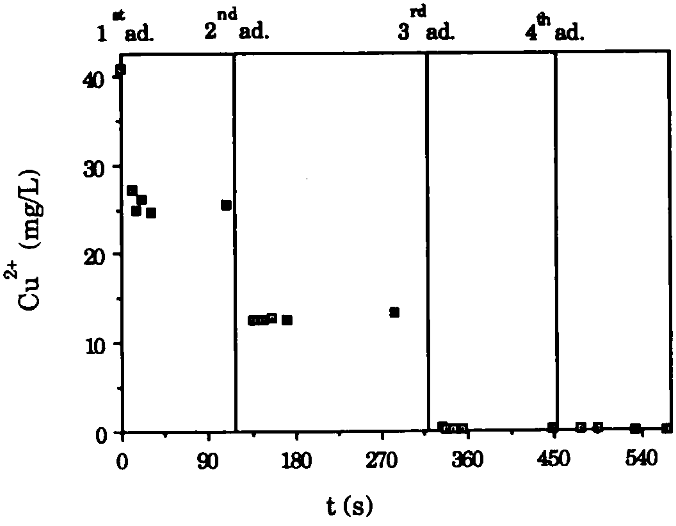


FIG. 8. [Cu^{2+}], pH (——), and redox potential (···) evolution in oxygen-free reactor at 10°C and 450 rpm for three additions of 110 μmol/L $NaBH_4$ and 215 μmol/L NaOH each as stabilized water solutions; $pH_0 = 6.0$; $[Cu^{2+}]_0 = 415$ μmol/L.



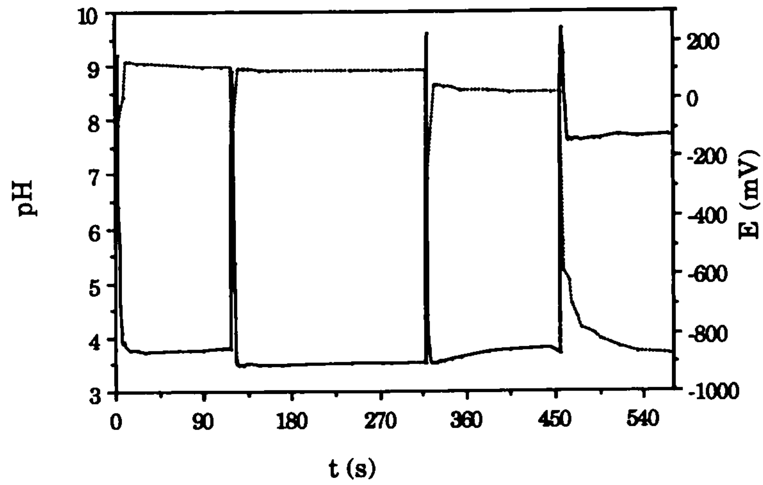


FIG. 9. $[Cu^{2+}]$, pH (——), and redox potential (···) evolution in oxygen-free reactor at 20°C and 450 rpm for four additions of 110 μmol/L $NaBH_4$ and 215 μmol/L NaOH each as stabilized water solutions; $pH_0 = 6.0$; $[Cu^{2+}]_0 = 640$ μmol/L.

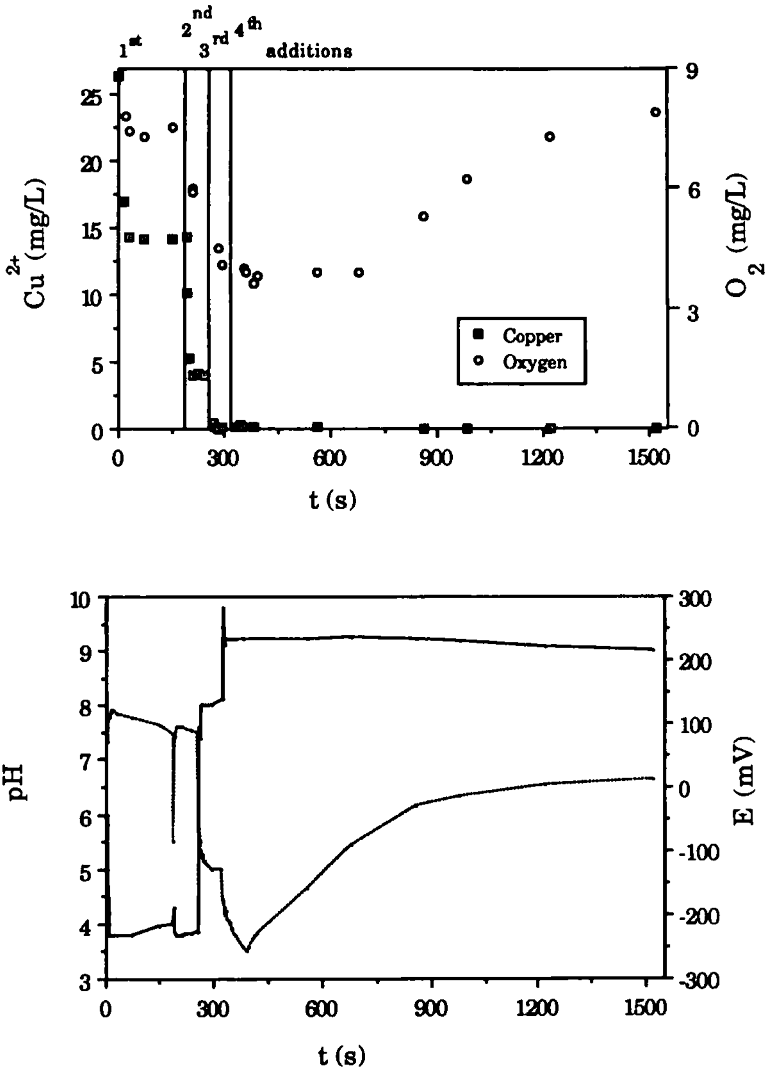


FIG. 10. [Cu^{2+}], dissolved oxygen, pH (——), and redox potential (···) evolution in unstoppered reactor at 20°C and 450 rpm for four additions of 110 μmol/L $NaBH_4$ and 215 μmol/L NaOH each as stabilized water solutions; pH_0 = 6.0; [Cu^{2+}]$_0$ = 415 μmol/L.

In an analogous way, the following overall equation for Cu^{2+} reduction to Cu_2O is obtained from Reactions (6) and (3):

$$2BH_4^- + Cu^{2+} + 6H_2O \rightarrow 2H_3BO_3 + \tfrac{15}{2}H_2 + \tfrac{1}{2}Cu_2O \qquad (11)$$

Equations (10) and (11) are in good agreement with the experimental BH_4^-/Cu^{2+} ratios needed to achieve complete Cu^{2+} removal when using solid $NaBH_4$. As indicated before, when using alkaline solution of $NaBH_4$, the addition of NaOH partially inhibits Reaction (3), leading to a substantially higher efficiency of borohydride in Cu^{2+} removal.

Borohydride consumption by Reactions (3) and (5) can be expressed by the kinetic equation:

$$\begin{aligned} -d[BH_4^-]/dt &= k_1[BH_4^-][H^+] + k_2[BH_4^-][Cu^{2+}] \\ &= [BH_4^-]\{k_1[H^+] + k_2[Cu^{2+}]\} \qquad (12) \end{aligned}$$

The Cu^{2+} reduction by Reaction (5) can be written as

$$-d[Cu^{2+}]/dt = 4k_2[BH_4^-][Cu^{2+}] \qquad (13)$$

Thus,

$$\frac{d[BH_4^-]}{d[Cu^{2+}]} = \frac{k_1[H^+] + k_2[Cu^{2+}]}{4k_2[Cu^{2+}]} \qquad (14)$$

At constant pH and complete exhaustion of borohydride, integration of Eq. (14) yields

$$[BH_4^-]_{ad} = C_1 \ln \frac{[Cu^{2+}]_0}{[Cu^{2+}]_e} + \tfrac{1}{4}\{[Cu^{2+}]_0 - [Cu^{2+}]_e\} \qquad (15)$$

$$C_1 = k_1[H^+]/4k_2 \qquad (16)$$

where $[BH_4^-]_{ad}$ corresponds to the amount of borohydride fed per unit volume, and $[Cu^{2+}]_0$ and $[Cu^{2+}]_e$ represent copper(II) concentrations at the initial moment and after BH_4^- exhaustion, respectively.

In a similar fashion, Eq. (17) can be obtained for Cu^{2+} reduction to Cu_2O:

$$[BH_4^-]_{ad} = C_2 \ln \frac{[Cu^{2+}]_0}{[Cu^{2+}]_e} + \tfrac{1}{8}\{[Cu^{2+}]_0 - [Cu^{2+}]_e\} \qquad (17)$$

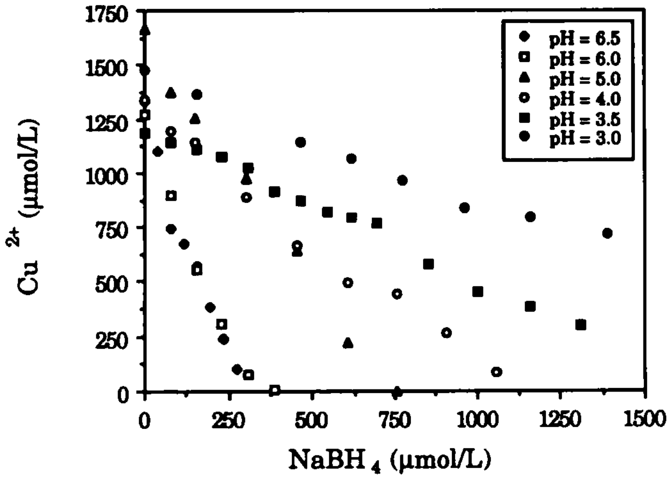


FIG. 11. [Cu^{2+}] versus NaBH$_4$ fed at different constant pH values.

$$C_2 = k_1[H^+]/8k_2' \tag{18}$$

Experiments were performed at different constant controlled pHs where NaBH$_4$ was fed very slowly as an alkaline solution by means of a microburette. This allows one to consider the BH_4^- concentration to be negligible at any time and any point in the reactor. Homogeneous copper(II) and pH distribution can thus be assumed. The results obtained are reported in Fig. 11. Fitting of the experimental values at each operating pH, by least squares, allows the values of the kinetic constants k_2 and k_2' to be obtained. These values are reported in Table 2. According to the Pourbaix diagram, it was assumed that metallic copper (k_2) is produced at pHs 3 and 3.5 whereas Cu_2O (k_2') is the reduced species at pHs 5, 6, and 6.5.

TABLE 2
Experimental Values Obtained for
k_2 and k_2' (L·mol^{-1}·s^{-1})

pH	k_2	k_2'
3.0	410,000	
3.5	95,000	
5.0		95,000
6.0		25,000
6.5		120,000

Even though the values obtained show some dispersion, they fall within the same order of magnitude in spite of the experimental difficulties of the system investigated and the assumptions made on the proposed model. In fact, it is not unlikely that some important catalytic and autocatalytic effects may be present. It should also be noted that the values of the constants k_2 and k_2' are highly sensitive to slight errors in Cu^{2+} concentrations. Nevertheless, the model provides valid information on the relative rates of the two competitive reactions (Cu^{2+} and water reduction) considered. If one takes a value of 770,000 ($L\cdot mol^{-1}\cdot s^{-1}$) for the kinetic constant of water reduction at 20°C, both rates will be similar when Cu^{2+} and H^+ concentrations are similar, which is in good agreement with the values of the pH obtained after stabilization following each addition of borohydride in the experiments presented in Figs. 2–9. Results obtained at higher Cu^{2+} initial concentration ($\approx$ 275 mg/L) also proved to be consistent with this, leading to lower stabilized pH values fairly close to those theoretically expected.

Some conclusions of practical interest can be pointed out from the results obtained: Alkaline pHs should be maintained, and a fairly efficient mixing system has to be used in order to optimize the efficiency of borohydride in Cu^{2+} removal. Previous removal of dissolved oxygen is also recommended. Increasing the borohydride dose will not only have an important negative effect on the economy of the process but will also lead to a detrimental stabilization of precipitate particles in suspension due to released H_2. Moreover, the final boron concentration in the treated waste is an important point to be considered in this technique. A final polishing treatment to remove residual boron from the effluent would be necessary in most cases, and the corresponding additional cost must be considered.

Acknowledgments

The authors want to acknowledge the Spanish CICYT which provided financial support for this work through Project PA 86/0088 and a grant to C.G.-L. We appreciate the helpful advice of Dr. David J. Wilson of Vanderbilt University in the revision of the manuscript. We also acknowledge Ventron Thiokol for kindly providing technical information.

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Received by editor September 30, 1991