COBALT(II) REMOVAL FROM WATER BY CHEMICAL REDUCTION WITH SODIUM BOROHYDRIDE

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Abstract—The stoichiometry and kinetics of Co²⁺ reduction with NaBH₄ in aqueous solution have been studied. A substantial excess of borohydride is needed to achieve complete Co²⁺ removal from water, mainly due to borohydride consumption in the BH₄⁻/H₂O reaction unless the pH is sufficiently alkaline. In this case, cobalt precipitation occurs mainly as Co(OH)₂. Absence of dissolved oxygen in the reactor is required to avoid rapid reoxidation of reduced cobalt. The elemental analysis of the reduced species is consistent with Co₂B. The ease of sludge reoxidation and the final boron concentration in the effluent resulting from the needed excess of borohydride are serious disadvantages of this technique for Co²⁺ removal. A kinetic model has been proposed to describe the behaviour of the system. The model reproduces reasonably well the experimental results, although some discrepancies were observed in the early stages of the process. These can be mainly attributed to mass-transfer limitations.

Key words—cobalt(II), borohydride, cobalt boride, chemical reduction, precipitation, kinetic model, redox reactions

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>growth factor of k₆ [defined in equation (10)]</td>
</tr>
<tr>
<td>k₆</td>
<td>rate of H⁺ production from boric acid dissociation</td>
</tr>
<tr>
<td>K₀</td>
<td>rate of H⁺ production from water dissociation</td>
</tr>
<tr>
<td>Kₛ</td>
<td>first dissociation constant for boric acid [defined in equation (11)]</td>
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<td>Kₛ</td>
<td>solubility product of Co(OH)₂ [defined in equation (12)]</td>
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<td>K₆</td>
<td>water ionic product [defined in equation (13)]</td>
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<td>k₁</td>
<td>kinetic constant [defined in equation (6)]</td>
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<td>k₆</td>
<td>kinetic constant [defined in equation (8)]</td>
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<tr>
<td>k₇</td>
<td>kinetic mass transfer coefficient for oxygen [defined in equation (9)]</td>
</tr>
<tr>
<td>k₈</td>
<td>kinetic mass transfer coefficient for oxygen in absence of chemical reaction [defined in equation (10)]</td>
</tr>
<tr>
<td>Oh</td>
<td>rate of OH⁻ production from Co(OH)₂ dissociation</td>
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Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε</td>
<td>efficiency of borohydride use (mole of Co²⁺ removed per mole of NaBH₄ added)</td>
</tr>
<tr>
<td>μ</td>
<td>rate of cobalt boride reoxidation following equation (5)</td>
</tr>
<tr>
<td>φ</td>
<td>rate of borohydride consumption following equation (2)</td>
</tr>
<tr>
<td>Ω</td>
<td>rate of cobalt(II) removal following equation (4)</td>
</tr>
</tbody>
</table>

INTRODUCTION

Conventional alkaline precipitation as an end-of-pipe metals control technology for industrial wastewaters treatment before effluent discharge performs reasonably well in most cases in achieving regulatory standards. The subsequent sludge handling and disposal involves some problems due to the high leachability of these substances. Alternative methods are being developed which focus more on detoxification of sludges or on waste avoidance or minimization by metals recovery, rather than on achieving a higher quality effluent. Of course, this latter would also be welcome. Two of these recovery technologies are ion exchange and reverse osmosis, both of which can reach high quality effluents and a concentrated stream that in some cases may be reused in the production cycle. Also, reductive electrolysis is used to recover spent metals from wastewaters, but capital costs may be high and high concentrations are required for the process to work at acceptable efficiencies.

Chemical reduction and precipitation has low capital costs and is easily done. It results in ion reduction, usually to the metallic state, with a marked improvement in physical and chemical sludge characteristics. Sodium borohydride is a mild but very effective reducing agent, with a low equivalent weight (eq. weight = 4.7 g/eqiv.) and a high reduction potential (E° = -1.23 V). The general reaction for reduction of divalent metallic ions to the metallic state is:

\[
\text{BH}_4^- + 4 \text{Me}^{2+} + 3 \text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 + 4 \text{Me}^0 + 7 \text{H}^+ \
\]

(1)

Table 1 shows the theoretical weight ratios that may be achieved from equation (1). When other oxidants are present borohydride will also be consumed in competitive reactions involving these species. Most of these, like dissolved oxygen, may be
previously removed with cheaper reducing agents (i.e. sodium dithionite). However, in aqueous systems one major problem will arise from the reduction of water by borohydride given by reaction (2). The kinetics of this reaction, at pH values below 9, follows equation (3) where the preexponential factor is given in (1·mol⁻¹·s⁻¹), according to literature data (Levine and Kreevoy, 1972; Kreevoy and Hutchins, 1972).

\[ \text{BH}_4^- + 3 \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_2\text{BO}_3^- + 4 \text{H}_2 \quad (2) \]

\[ \frac{d[\text{BH}_4^-]}{dt} = 6.62 \times 10^{13} \text{e}^{-\left(\frac{4000}{\text{RT}}\right)}[\text{H}^+][\text{BH}_4^-] \quad (3) \]

Work on heavy metals removal from water effluents using sodium borohydride has been reported in the literature, and includes industrial case histories. According to those reports the technique is reliable at controlled neutral/alkaline pH values for precious and noble metal ions like silver, mercury, copper and lead (Rosenzweig, 1971; Cook et al., 1979; Cushnie, 1983; Lindsay et al., 1985; Patrick et al., 1987) although there is still some lack of fundamental information regarding the borohydride/metal systems. This lack is more substantial in the case of other heavy metals with higher oxidation potentials. Ying et al. (1987) has reported interesting work on nickel and Cook et al. refers to the removal of cadmium in a silver cadmium effluent. Nevertheless, further investigation is required with regard to these types of metals to establish the applicability of the method. The present focuses on the study of the stoichiometry and kinetics of Co²⁺ reduction with sodium borohydride. The experimental conditions are restricted to a range of initial pH values in which no precipitation of Co²⁺ as hydroxide takes place.

The redox potential of the Co²⁺/Co⁰ pair \((E^\circ = -0.28 \text{V})\) makes a general knowledge of the behaviour of the Co²⁺/BH₄⁻ system of interest. Previous work on Cu²⁺ \((E^\circ = 0.34 \text{V})\) revealed some limitations of the borohydride reduction technique (Gomez-Lahoz, 1991; Gomez-Lahoz et al., 1992), although this technique is effective with Cu²⁺. On the other hand, when this method was tested to reduce Zn²⁺ \((E^\circ = -0.76)\) a rapid reoxidation of the reduced species of zinc by water was observed which prevents the use of the technique with zinc (Gomez-Lahoz, 1991).

Cobalt(II) does not follow equation (1) when reacting with NaBH₄, but forms a boride of mixed stoichiometry, generally expressed as CoₓB. (Heizman and Ganem, 1982; Osby et al., 1986). The reaction may be written as:

\[ \text{BH}_4^- + 2 \text{Co}^{2+} \rightarrow \text{Co}_2\text{B} + \frac{1}{2}\text{H}_2 + 3 \text{H}^+ \quad (4) \]

and the theoretical weight ratio for cobalt reduction by this reaction is one half that given in Table 1.

### Table 1. Theoretical weight ratios of reduced metal obtainable from ionic species with sodium borohydride based on reaction (1).

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Weight ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd²⁺</td>
<td>1</td>
</tr>
<tr>
<td>Co³⁺</td>
<td>6</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>7</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>23</td>
</tr>
<tr>
<td>Fe⁺⁺</td>
<td>22</td>
</tr>
<tr>
<td>Hg⁺⁺</td>
<td>21</td>
</tr>
<tr>
<td>Hg⁺</td>
<td>42</td>
</tr>
<tr>
<td>Ni⁺⁺</td>
<td>6</td>
</tr>
</tbody>
</table>

*Weight ratio = maximum g of metal reduced/g of NaBH₄.

Simulated wastewaters were prepared using deionized water with conductivity values < 5 µmhos/cm. The necessary amount of a previously prepared solution of CoCl₂·6H₂O containing 1000 mg Co²⁺/l was added to obtain the desired initial concentrations of cobalt(II). Dilute HCl or NaOH were 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, taking, for the experiments that were performed with solid borohydride, amounts of approximately 10 g. These were placed in a second desiccator, from which was weighed the necessary amount for each experiment. Stabilized water solutions of sodium borohydride were prepared with different concentrations of NaOH, and maintained at temperatures below 10°C. The reducing capacity of the borohydride solution was measured immediately before use by the Lyttle method (Lyttle et al., 1937). 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 batchwise in a 2.35 l cylindrical bottom-rounded 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 HI8343 oxyimeter. 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 preliminary 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 system was chosen after previous experiments with cellulose filters, where Co²⁺ adsorption was observed, and with fritted-glass filters of 10–20 µm pore width, which showed filtering rates substantially lower than needed to obtain the desired 10–20 samples per minute. Cobalt analyses were performed by atomic absorption spectrophotometry (AA) with a Varian AA-475 instrument. The precipitate was dissolved in HNO₃ and analyzed for cobalt and boron by AA and the curcumine method (APHA, 1975), respectively.

### EXPERIMENTAL

The Pourbaix diagram for cobalt at 10 and 40 mg/l is presented in Fig. 1. As indicated before, the reduced species of cobalt with NaBH₄ has been reported in the literature as a boride of mixed stoichiometry, generally expressed as CoₓB. This stoichiometry is in agreement with the cobalt and boron...
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Fig. 1. Pourbaix diagram for cobalt: [Co²⁺] of 40 (---) and 10 (...) mg/l. Oxidation potentials referred to the Ag/AgCl/KCl(3M) electrode.

analyses of our precipitate. Nevertheless, thermodynamic data are not available and this species has not been included in the diagram. More recently Kim and Brock (Kim and Brock, 1987) studied the precipitate by ICP-AES and XPS and concluded that it consists most probably of a metallic cobalt/boron admixture rather than a metal boride. The redox potential values for precipitate formation observed in our experiments falls in the vicinity of that corresponding to the formation of metallic cobalt. Thus the Pourbaix diagram given in Fig. 1 may be reasonably valid for practical purposes. According to it a redox potential of −600 mV is needed to accomplish Co²⁺ reduction. The H₂/O⁺ equilibrium line shows that Co⁰ may be reoxidized by H₂O at pH lower than 7. Other oxidant species, such as dissolved oxygen, may undergo reaction with borohydride as well as with the reduced cobalt species. Previous experiments allowed us to neglect the contribution of the NaBH₄/O₂ reaction due to its slow rate (Gomez-Lahoz, 1991; Gomez-Lahoz et al., 1992). Nevertheless, the reoxidation of reduced cobalt by dissolved oxygen has to be considered. This reaction can be written as:

Co₂B + 7/4 O₂ + 4 H⁺ →

2Co²⁺ + H₃BO₃ + 1/2 H₂O (5)

Figure 2 shows the variation of Co²⁺ concentration, dissolved oxygen, pH and redox potential with time in an experiment performed in an unstoppered stirred reactor using excess borohydride. There is an initial period in which no cobalt precipitation takes place. Most likely, reduced cobalt is undergoing immediate reoxidation, as suggested by the dissolved oxygen decrease during this period. The increase of pH during this stage can be explained by the borohydride/water reaction and cobalt reoxidation [equations (2) and (5), respectively]. This initial period is followed by a smooth decrease in dissolved Co²⁺, most probably due to Co(OH)₂ formation, given the pH values. As dissolved oxygen is ex-

hausted, Co²⁺ reduction takes place rapidly, giving rise to a sharp decrease in Co²⁺ concentration, pH and potential values. A blackish precipitate was clearly observed in the reactor at this stage. The Co²⁺ concentration reaches a minimum and subsequently an increase is observed, coincident with a similar trend in the pH and potential curves. Borohydride exhaustion in the aerated reactor leads to a predominance of cobalt reoxidation. The Co²⁺ concentration stabilizes finally, due to insoluble Co(OH)₂ formation. Analogous trends were observed in a run performed under similar operating conditions but using higher Co²⁺ and borohydride doses (760 and 1420 µmol/l), respectively). The initial induction period for Co²⁺ removal was substantially shorter, consistent with the higher cobalt and borohydride concentrations used in this experiment.

An experiment fairly similar to the one reported in Fig. 2 was carried out in an oxygen-free stoppered reactor. The results are shown in Fig. 3. In the absence of dissolved oxygen Co²⁺ reduction takes place rapidly. The initial stages of the pH curve, which were verified to be oscillatory, can be explained as a result of mass-transfer limitations occurring during the early period after the borohydride was fed. This was confirmed by flow-pattern experiments using NaOH and solid NaBH₄ (Gomez-Lahoz, 1991; Gomez-Lahoz et al., 1992). The initial pH increase in Fig. 3 is attributed to a high local excess

Fig. 2. [Co²⁺], [O₂], pH (---) and redox potential (...) evolution with time in unstoppered reactor at 20°C and 450 rpm; pH₄ = 6.0; [Co²⁺]₀ = 475 µmol/l; [NaBH₄]₀ = 900 µmol/l, added as solid.
of borohydride leading to predominance of the BH₄⁻/H₂O reaction. As the local BH₄⁻ concentration decreases and pH increases this reaction slows and a sharp drop in the pH curve is registered consistent with Co²⁺ reduction. Further water reaction with excess borohydride once the Co²⁺ concentration reaches a low level leads to a pH increase.

To establish the BH₄⁻/Co²⁺ molar ratio needed to achieve complete Co²⁺ reduction we performed several experiments at the operating conditions described in Fig. 3 but using different NaBH₄ doses. In these runs the reactant fed was partitioned into several additions. We previously confirmed that the final results were not dependent on the number of additions of borohydride but only on the total amount fed. A representative example of these experiments is reported in Fig. 4. The results obtained allow one to conclude that a molar ratio close to 2.4 was necessary for complete Co²⁺ removal; this ratio means about 9.5 times more borohydride than the theoretical dose calculated for Co²⁺ reduction to metallic cobalt given in Table 1. Nevertheless, as indicated before, Co²⁺ reduction follows equation (4) forming Co₃B. With respect to the stoichiometry of this latter reaction the required BH₄⁻/Co²⁺ molar ratio represents a borohydride excess of 380% above the stoichiometric requirement. This is due to the occurrence of the borohydride/water reaction to an important extent. To avoid this, rather alkaline pHs would be needed, but in that case a Co(OH)₂ precipitate would be obtained.

Figure 5 shows the results obtained in an experiment carried out under operating conditions fairly similar to those reported in Fig. 4 but in which NaBH₄ was added as an alkaline stabilized solution. The efficiency of borohydride use (ε = mole of Co²⁺ removed per mole of NaBH₄ added) after the two first additions is now ε = 0.55 vs ε = 0.45 when one uses solid NaBH₄. This improvement is substantially less significant than the observed for copper (Gomez-Lahoz, 1991; Gomez-Lahoz et al., 1992). There the use of stabilized alkaline solution showed an important advantage over solid NaBH₄, allowing one to increase ε from 0.84 to 2. The NaOH concentration in the stabilized borohydride solution was found to be the main factor in efficiency improvement, due to the inhibition of the borohydride/water reaction in the early stages following NaBH₄ feed. In the case of cobalt we used NaOH/BH₄⁻ molar ratios in the stabilized solution that were 10 times lower than those used for the copper experiments to avoid Co(OH)₂ formation prior to Co²⁺ reduction. This problem did not arise in the case of Cu²⁺ due to the higher initial rate of copper reduction.

Although pH is a very important variable with regard to the process studied, initial pH showed no significant effect on borohydride efficiency within the...
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The reduced cobalt species, Co₂B, has been reported in the literature to catalyze the borohydride/water reaction (Schlesinger, 1953; Kaufman, 1985). Our experimental results suggest as well an autocatalytic effect of Co₂B on Co²⁺ reduction. According to this, the rate of Co²⁺ consumption from reaction (4) may be expressed by:

\[
\Omega = \frac{d[Co^{2+}]}{dt} = k_1[Co^{2+}][BH₄⁻]
+ k_2[Co^{2+}][Co₂B]
\]

The rate of borohydride consumption from the borohydride/water reaction might be written as:

\[
\phi = \frac{d[BH₄⁻]}{dt} = k_3[Co^{2+}][H⁺]
+ k_4[Co²⁺][H⁺][Co₂B]
\]

In an unstoppered reactor, Co₂B reoxidation by dissolved oxygen was found to be significant, causing the induction period seen in Fig. 2. The rate of Co₂B consumption by reaction (5) may be expressed by:

\[
\mu = \frac{d[Co₂B]}{dt} = k_5[Co₂B][O₂]
\]

Oxygen is absorbed from air at a rate given by:

\[
\frac{d[O₂]}{dt} = k_6([O₂]_{in} - [O₂])
\]

An experimental value of 1.25 × 10⁻³ s⁻¹ has been obtained for k₆ at the stirring velocity used in all the mildly acidic values investigated in this work, as can be seen from Figs 5 and 6. In fact when one starts at pH 5 the expected additional BH₄⁻ consumption to reach pH 6 should be no more than 10 μmol/l.

The effect of temperature can be observed from Figs 5 and 7, where all other operating conditions are identical. A decrease in the initial Co²⁺ reduction rate can be noticed when temperature is lowered from 20 to 10°C, giving rise to an induction period of about 40 s after which the results obtained become fairly similar to those at the higher temperature.

Increasing the initial Co²⁺ concentration to ≈ 40 mg/l showed little effect on borohydride efficiency, as can be seen from Figs 5 and 8. The resulting φ values for the first addition are 0.60 and 0.66 respectively. The pH curve in Fig. 8 shows somewhat lower stabilization values consistent with the higher cobalt(II) concentrations.

Model proposal

The reduced cobalt species, Co₂B, has been reported in the literature to catalyze the borohydride/water reaction (Schlesinger, 1953; Kaufman, 1985). Our experimental results suggest as well an autocatalytic effect of Co₂B on Co²⁺ reduction. According to
The concentration values in equations (11)–(13) are calculated from the following relationships:

\[
[H^+]_{t+\Delta t} = [H^+]_t + \frac{1}{2} \Omega - \phi - 4\mu + h_{\text{aq}} + h_a \Delta t
\]  
(14)

\[
[OH^-]_{t+\Delta t} = [OH^-]_t + [h_a + oh_b] \Delta t
\]  
(15)

\[
[H_2BO_4^-]_{t+\Delta t} = [H_2BO_4^-]_t + [h_a + h_a] \Delta t
\]  
(16)

\[
[H_3BO_3]_{t+\Delta t} = [H_3BO_3]_t + [\phi + \mu - h_a] \Delta t
\]  
(17)

\[
[Co^{2+}]_{t+\Delta t} = [Co^{2+}]_t + (2\mu + \Omega + \frac{1}{2}oh_b) \Delta t
\]  
(18)

where \( h_{\text{aq}} \) and \( h_a \) represent the rate of \( H^+ \) production following equilibria (11) and (13) respectively and \( oh_b \) is the rate of \( OH^- \) production according to equilibrium (12).

The following values were obtained for the kinetic constants used in the model:

\[
k_1 = 51 \text{ mol}^{-1} \text{ s}^{-1}
\]

\[
k_2 = 7.5 \times 10^8 \text{ mol}^{-2} \text{ s}^{-1}
\]

\[
k_3 = 7.7 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}
\]

\[
k_4 = 10^6 \text{ mol}^{-2} \text{ s}^{-1}
\]

\[
k_5 = 5 \times 10^4 \text{ mol}^{-1} \text{ s}^{-1}
\]

\[
k^* = 1.25 \times 10^{-3} \text{ s}^{-1}
\]

\[G = 10^3 \text{ mol}^{-1}
\]

The model described by equations (6)–(10) has been integrated using the fourth-order Runge–Kutta method. A Turbobasic program was written and run on a microcomputer equipped with an 80286 microprocessor and running MS-DOS. A variable time increment is implemented in the program and at each of the four integration steps in the Runge–Kutta method the following equilibrium equations are satisfied:

\[
K_{we} = \frac{[H_2BO_4^+][H^+]}{[H_2BO_3^-]} \tag{11}
\]

\[
K_c = [Co^{2+}][OH^-]^2 \tag{12}
\]

\[
K_a = [H^+][OH^-] \tag{13}
\]

where the corresponding values of \( K_{we}, K_c, \) and \( K_a \) are well known.
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Figures 9 and 10 show the results obtained from the model using the initial conditions of the experiments reported in Figs 2 and 4, respectively. As can be seen, the model reproduces fairly well the Co²⁺, pH and dissolved oxygen curves obtained in the run performed in an unstoppered reactor (Figs 2 and 9). Regarding the experiments carried out in an oxygen-free stoppered reactor, good predictions of the final Co²⁺ concentration and pH values are obtained. The discrepancies observed during the early stages after each borohydride addition may result from the assumption of instantaneous homogeneity of concentration made in the model, whereas mass-transfer limitations were found in practice as indicated before. Thus, more sophisticated experiments would be required to follow the behaviour of the system within the initial stages of the process.

CONCLUSION

Some conclusions of practical interest can be pointed out from the results obtained: Complete reduction of Co²⁺ with this technique requires a substantial excess of borohydride. Absence of dissolved oxygen in the reactor is needed to avoid reoxidation of the reduced cobalt. Optimization of borohydride efficiency in Co²⁺ removal would require a control of pH above the neutral point. Although a fairly well settleable sludge is obtainable, it becomes easily oxidizable giving rise to lixiviation problems. This, together with the final boron concentration in the effluent, derived from borohydride excess, limits seriously the utility of this method as a competitive technique for Co²⁺ removal.

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