1. Introduction

Acid mine drainage (AMD) is acid water generation due to chemical action of oxygen and atmospheric humidity on sulfide minerals - strongly associated with coal exploration. Permeable reactive barrier (PRB) is an alternative process to the treatment of groundwater contaminated by AMD. One of the first substances to be used in PRBs for groundwater remediation was zero-valent iron (ZVI). This reagent can be prepared with the help of sodium borohydride, $\text{NaBH}_4$, and iron chloride. This work aimed to study the fundamentals for the synthesis of ZVI from Fe-Cl aqueous solutions and the immobilization of metal ions with ZVI with the assistance of a “computational thermodynamics” tool. A concise experimental evaluation covering the preparation of ZVI as well as the reduction of Cu, Ni, and Al ions followed the theoretical analysis.

KEY WORDS: ZVI synthesis; $\text{NaBH}_4$; AMD; PRB; Computational thermodynamics.

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problems related to the groundwater contamination in areas which can influence aquifers are of major concern[3].

Permeable reactive barriers (PRB) are in situ treatment zones that passively capture a plume of contaminants and (i) remove (immobilize); or (ii) break down the contaminants, releasing uncontaminated water. They have been developed during the last two decades of the 20th century as an alternative treatment for AMD contaminated groundwater[4,5].

Besides being one of the first substances to be used in PRBs for groundwater remediation, zero-valent iron (ZVI) shows a larger capacity in comparison with conventional compounds for the sequestration of metal ions from water[6–8].

A reducing agent which can be used for the production of ZVI, both in the laboratory and on a technical scale, is sodium borohydride (also known as sodium tetrahydrodiborate) - an inorganic compound with the formula NaBH4. ZVI is prepared via reduction of ferric iron by adding to an aqueous solution of FeCl3·6H2O an aqueous solution of NaBH4.

The purpose of this work is to study the fundamentals of sodium borohydride hydrolysis for the synthesis of ZVI from iron chloride aqueous solutions, and the immobilization (reduction) of selected metal ions with ZVI. Both themes are covered with the assistance of a "computational thermodynamics" tool.

A concise experimental evaluation covering the preparation of ZVI as well as the reduction of Cu, Ni, and Al aqueous ions followed the theoretical analysis.

2. Theoretical Considerations

2.1 Hydrolysis of Sodium Borohydride

When added to water, solid sodium borohydride undergoes hydrolysis giving solid NaBO2 and gaseous hydrogen as products.

The conversion of hydrogen from water into hydrogen gas is of such importance that this substance is highly considered when it comes to the production and storage of hydrogen for electricity generation through fuel cells. In such case the term “steam hydrolysis” is used:

\[ \text{NaBH}_4 + 2 \text{H}_2\text{O} \rightarrow 4 \text{H}_2(g) + \text{NaBO}_2 \]  

(1)

Ideally, 2 moles of water are required to liberate 4 moles of gaseous hydrogen; in practice, excess water is used because the solid by-product can exist with a varying degree of hydration (i.e. hydrated metabolates); the term “x” in Equation 2 accounts for excess water[9].

\[ \text{NaBH}_4 + (2 + x) \text{H}_2\text{O} \rightarrow 4 \text{H}_2(g) + \text{NaBO}_2 \cdot x \text{H}_2\text{O} \]  

(2)

Since the middle of the 20th century[10] it is known that the release of hydrogen makes sodium borohydride also a strong water soluble reducing agent - in which case it can be used in the electroless production of metals from their ions. The importance of NaBH4 in this work lies exactly on this particular aspect.

In order to promote the reduction of aqueous ferric and ferrous ions into ZVI, the addition of a strong reducing agent to the water is mandatory. The iron produced by this method tends to come out in the form of fine-grained loose particles - often nano-sized -, a factor which is very important for the intended use. Added to water, NaBH4 undergoes hydrolysis - also called self-hydrolysis, to differentiate it from hydrolysis in the presence of a catalyst. This is usually represented by stoichiometric reactions such as[11–13]:

\[ \text{NaBH}_4 + 2 \text{H}_2\text{O} = 4 \text{H}_2(g) + \text{NaBO}_2(\text{aq}) \]  

(3)

\[ \text{NaBH}_4 + 4 \text{H}_2\text{O} = 4 \text{H}_2(g) + \text{NaOH(\text{aq})} + \text{H}_3\text{BO}_3 \]  

(4)

\[ \text{NaBH}_4 + 4 \text{H}_2\text{O} = 4 \text{H}_2(g) + \text{Na(\text{OH})}_4(\text{aq}) \]  

(5)

The reaction mechanism is multifaceted and pH-dependent. In view of the fact that the reaction by product is basic, pH rises and reaction slows.

2.2 Electroless Deposition of Iron

To explain the reduction of the iron ions, some stoichiometric reactions are referred to in the literature, e.g.[14–16]:

\[ \text{Fe}^{2+} + 2 \text{BH}_4^{-} + 6 \text{H}_2\text{O} = \text{Fe}^{0} + 2 \text{B(\text{OH})}_3 + 7 \text{H}_2 \]  

(6)

\[ \text{Fe}^{3+} + 3 \text{BH}_4^{-} + 9 \text{H}_2\text{O} = \text{Fe}^{0} + 3 \text{H}_3\text{BO}_3 + 12 \text{H}^{+} + 6 \text{H}_2 \]  

(7)

\[ \text{Fe(H}_2\text{O)}_6^{2+} + 3 \text{BH}_4^{-} + 3 \text{H}_2\text{O} = \text{Fe}^{0} + 3 \text{B(\text{OH})}_3 + 10.5 \text{H}_2 \]  

(8)

3. Methodology

3.1 Thermodynamic Simulations

Fact53 (FS53Base.cdb) general compound database was used with FactSage version 6.1 software, in order to carry out the calculations. This database contains selected data for over 4,500 compounds taken from standard compilations as well as most of the data for those compounds which have been evaluated and optimized to be thermodynamically consistent with other “Fact databases”.

Despite the use of the term “compound” in association with this database, it contains also data for two solutions (which are the gaseous and aqueous phases). Boron containing ions and aqueous compounds used in the present work can be seen in Box 1.

Box 1  Aqueous and ionic species containing boron present in FACT53 database

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH4[-]</td>
<td></td>
</tr>
<tr>
<td>HBO2[-]</td>
<td></td>
</tr>
<tr>
<td>B(OH)3[-]</td>
<td>(H2O)3</td>
</tr>
<tr>
<td>B(OH)4[-]</td>
<td></td>
</tr>
<tr>
<td>H3BO3[-]</td>
<td></td>
</tr>
<tr>
<td>H3BO3(aq)</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Experiments

The experimental analysis included both ZVI production and precipitation (immobilization) of metal ions from water.
All chemicals used were reagent grade and water was de-ionized. NaBH₄ (Vetec) and FeCl₂·6H₂O (Vetec) were used to prepare ZVI. The synthesized iron was subsequently in metal ion sequestration experiments.

Metal salts to emulate AMD solution consist of CuSO₄·5H₂O (Labsynth), NiSO₄·6H₂O (Labsynth), and Al₂(SO₄)₃·(14–18)H₂O (Vetec).

4. Results and Discussion

4.1 NaBH₄ Hydrolysis

The dissolution of NaBH₄ in water was simulated by adding to the system sodium borohydride in amounts varying from 1x10⁻⁴ to 1 g per liter of water.

The simulation results can be seen in Fig. 1. Of all species containing boron present in the Fact53 database (see methodology), only three have significance (one of them is a non-ionic species). BO₂⁻ is the most abundant at the higher end of the NBH₄ amount range, while H₃BO₃(aq) takes this position on the other extremity. The third is the monovalent anion H₂BO₃⁻.

Fig. 1 Activity of aqueous solution constituents as a function of the logarithm of NaBH₄ amount added to 1 L water; B-containing constituents are displayed as black symbols (FactSage).

4.2 Stoichiometric Reactions

Using Fact53 database, the simplest stoichiometric reaction which can be written is:

NaBH₄ + 2 H₂O = 4 H₂(g) + Na⁺ + BO₂⁻  \hspace{1cm} (9)

In order to take into account the production of the H₃BO₃ and H₃BO₃(aq), a new decomposition reaction was written:

2 NaBH₄ + 7 H₂O = 8 H₂(g) + 2 Na⁺ + H₃BO₃⁻ + H₃BO₃(aq) + OH⁻ \hspace{1cm} (10)

The overall reaction, then, becomes:

3 NaBH₄ + 9 H₂O = 12 H₂(g) + 3 Na⁺ + H₂BO₃⁻ + H₂BO₃(aq) + OH⁻ + BO₂⁻ \hspace{1cm} (11)

4.3 Pourbaix Diagram

Overlaying the electrochemical potential determined for every amount of NaBH₄ added to 1 L water as a function of pH over the Pourbaix diagram for iron, it is possible to see the strong reducing effect of sodium borohydride addition to water (Fig. 2).

Under these circumstances, the chances are that Fe⁰ becomes the only solid phase to come out in the equilibrium state. Nevertheless, this fact certainly should be attributed to reaction kinetics - once the thermodynamic simulation results predicts only the presence of iron compounds. Given that hydroxides (or oxides) are composed of several atomic species ordered in a crystal lattice, this may have a certain role in the crystallization process, delaying the precipitation of these solids, to the benefit of pure iron precipitation.

Fig. 2 Electrochemical potential as a function of pH for selected amounts of NaBH₄ added to 1 L water overlaying the Pourbaix diagram for iron (FactSage).

4.4 Electroless Deposition of Iron

The electroless reduction of iron ions was simulated simply by adding to a plain solution of Fe and Cl ions in water a certain amount of solid NaBH₄.

The addition of sodium borohydride to ferric chloride and ferrous chloride aqueous solutions containing each 0.005 [mole] of reactant can produce different results. When the amount of NaBH₄ added to the water is small, the ratio Cl/Fe is of importance: for a high Cl/Fe ratio (use of reactant FeCl₃), chloride ions tend to stabilize the iron ions in solution, causing no ZVI precipitation. This effect lessens for higher NaBH₄ amounts (Table 1).

Interesting to note, iron ions reduction by BH₄⁻ - as cited in the literature (see text, Section 2.2) - cannot be confirmed by the simulations, since its activity in the aqueous solution is very small - always < 1x10⁻⁵⁰ - even after the addition of 10 g NaBH₄ to the water.
Table 1 Percentage of ZVI (mass basis, Fe total mass is 0.273 g) for two amounts of NaBH₄ added to a solution containing 0.005 mole FeCl₂ (or FeCl₃) in 1 L water (FactSage)

<table>
<thead>
<tr>
<th>Amount of NaBH₄</th>
<th>1 [g]</th>
<th>10 [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>with FeCl₂</td>
<td>21.1</td>
<td>94.2</td>
</tr>
<tr>
<td>with FeCl₃</td>
<td>0.0</td>
<td>91.4</td>
</tr>
</tbody>
</table>

4.5 Immobilization of Metals

The experimental efficacy of ZVI for the immobilization of Cu, Ni, and Al cations from AMD has been verified with some simulations. To approximate simulation (and experiments) to reality, sulphates of the chosen metals were used: CuSO₄, NiSO₄, and Al₂(SO₄)₃. Based on knowledge of AMD composition, three concentrations were chosen: 50 mg/L, 200 mg/L, and 130 mg/L, respectively. Later, these values were adjusted to 54 mg/L, 217 mg/L, and 132 mg/L in order to reproduce actual values used experimentally. Results show that thermodynamics predicts the complete removal of Cu, Ni, and Al cations from AMD (Table 2).

As it can be seen, precipitates resulting from simulated treatment of solutions with 2 g/L sodium borohydride are simple and complex sulfides and hydroxides – depending on the metal – and reproduce fairly well the experimental results obtained after five days of contact time.

5. Conclusions

A new stoichiometric Reaction 11 for sodium borohydride hydrolysis was suggested, and is reproduced below:

$$3 \text{NaBH}_4 + 9 \text{H}_2\text{O} = 12 \text{H}_2\text{O} + 3 \text{Na}^+ + \text{H}_2\text{BO}_3^- + \text{H}_3\text{BO}_3(aq) + \text{OH}^- + \text{BO}_2^-$$

Also, the importance of BH₄⁻ ion - frequently quoted in the literature - was not confirmed by the simulations, since the value of its activity is always very small. The addition of sodium borohydride to water produces simultaneously a pH increase and a redox potential decrease. With increasingly NaBH₄ amounts, this leads to the conditions required for the reduction of ferric or ferrous iron ions (production of ZVI) from aqueous chloride solutions. Nevertheless, from the thermodynamic point of view, this last situation is not reached within the used conditions.

As shown, from both theoretical (and experimental) results, ZVI particles can promote immobilization of dissolved Al, Cu, and Ni metal ions. The interaction of highly noble copper with ZVI is relatively notorious, since the cementation of aqueous copper ions with iron (scrap) is an established extractive metallurgical process. The cementation process, on the other hand, produces metallic copper which is not thermodynamically stable in water. Consequently, a copper-iron sulfide is obtained instead, according to the simulation results.

Nickel, with the standard electrode reduction potential of −0.25 V, is slightly more noble than iron, with −0.44 V, therefore, cementation of nickel ions is effective only if the electromotive force is high (as it happens with a much more reactive metal than ZVI, like Zn). For that reason, the removal of Ni is accomplished by the precipitation of nickel sulfide.

In view of the fact that Al is a very active metal, no metallic product is possible. Oxides and hydroxides, on the other hand, are very stable - thermodynamics predicts that alumina monohydrate precipitates even without iron addition (Table 2). Yet, for a reason not known up to now, all Al will precipitate as diaspore when ZVI is added to the solution.

NOTES

★ The United States Department of Energy (DOE) made a “no-go” decision in 2007 on the viability of aqueous NaBH₄ for its “FreedomCar” program (the solubility/crystallization issue was cited as a major concern); consequently many researchers have shifted focus toward the reaction involving solid NaBH₄ and steam.

References


Table 2 Percentage of metal precipitated (mass basis) before and after the addition of 2 g ZVI to a solution containing cations of Cu, Ni, and Al; thermodynamic and experimental results; experimental metal content remaining in solution after treatment are given for two elapsed time periods

<table>
<thead>
<tr>
<th>Metal</th>
<th>Initial amount [mg/L]</th>
<th>Percentage precipitated [wt.%] and phase (thermodynamic simulation)</th>
<th>Content remaining in solution [mg/L] (experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before*</td>
<td>Phase**</td>
</tr>
<tr>
<td>Cu</td>
<td>54</td>
<td>1.3</td>
<td>Cu(OH)₂(s)</td>
</tr>
<tr>
<td>Ni</td>
<td>217</td>
<td>0.0</td>
<td>Ni₃S₄(s)</td>
</tr>
<tr>
<td>Al</td>
<td>132</td>
<td>12.7</td>
<td>Al₂O₃(H₂O)(s)</td>
</tr>
</tbody>
</table>

* Refers to the addition of 2 g ZVI.

** Described following FACTS53 database.


