SYNTHESIS OF ZERO-VALENT IRON PARTICLES FOR ACID MINE DRAINAGE REACTIVE BARRIERS: EXPERIMENTAL STUDY AND THERMODYNAMIC EVALUATION[1]

Maria Alejandra Liendo[2]
Gelsa Edith Navarro Hidalgo[3]
Nestor Cezar Heck[4]
Carlos Hoffmann Sampaio[5]

Abstract

Acid mine drainage (AMD) is acid water generation due to the effect of oxygen and atmospheric humidity on sulfide minerals – strongly associated with coal exploration. Permeable reactive barriers (PRBs) is an alternative 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 $NaBH_4$. Aim of this work is 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.

Keywords: ZVI synthesis; Permeable reactive barriers; Thermodynamics

SÍNTESE DE PARTÍCULAS DE FERRO ZERO-VALENTE PARA BARREIRAS REATIVAS PARA DRENAGEM ÁCIDA DE MINAS: ESTUDO EXPERIMENTAL E AVALIAÇÃO TERMODINÂMICA

Resumo

A drenagem ácida de mina (DAM) é a geração de água ácida devida ao efeito do oxigênio e umidade atmosférica em sulfetos - fortemente associados com a exploração do carvão. Barreiras reativas permeáveis (BRPs) é uma alternativa para o tratamento de águas subterrâneas contaminadas pela DAM. Uma das primeiras substâncias a serem utilizadas em BRPs para remediação de águas subterrâneas foi ferro zero-valente, ZVI. Este reagente pode ser preparado com NaBH4. O objetivo deste trabalho é estudar os fundamentos para a síntese de ZVI de soluções aquosas de Fe-Cl, e a imobilização de íons metálicos com ZVI, com o auxílio de uma ferramenta de ‘termodinâmica computacional’. Uma avaliação experimental concisa relativa à preparação de ZVI, bem como à redução de íons Cu, Ni e Al foi feita na sequência da análise teórica.

Palavras-chave: Síntese ZVI, Barreiras reativas permeáveis; Termodinâmica

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[2] *MSc., Pos-Graduate Student, PPGEM, UFRGS*
[3] *Dra., LAPROM, PPGEM, UFRGS*
[4] *Dr., NTCm, PPGEM, UFRGS, heck@ufrgs.br*
[5] *Dr., LAPROM, PPGEM, UFRGS*

1 INTRODUCTION

Acid mine drainage (AMD) is the product resulting from the reaction of oxygen and water (or atmospheric humidity) with *sulfide minerals* (pyrite, marcasite) which can contaminate both ground and surface water.(1) Alongside with ferric, ferrous and sulphate ions, AMD normally presents metallic ions *e.g.* Mn, Al, Ni, Cu, Zn in different concentration. Depending on the case, these solutes can be harmful to the environment and inhabitants, therefore, a certain pressure exists for their removal or the reduction of their concentration.

Coal exploration is strongly associated with the presence of sulfide minerals. The identified coal resources in Brazil are situated in the Southern Region and sum up 32 billion tonnes. They spread out in Rio Grande do Sul, Santa Catarina, Paraná, and São Paulo States of which Rio Grande do Sul alone is responsible for 94% of all known resources so far.(2) After exploration, the area occupied by coal residues is normally large and the contamination of groundwater by AMD highly probable. In view of the escalating degradation of surface water resources (including the aquatic habitat), the possibility for utilization of aquifers as drinking water supplies is increasingly important. Consequently, 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 remove (immobilize) or break down the contaminants, releasing uncontaminated water. They have being developed during the last two decades of the 20th century as an alternative treatment for groundwater contaminated by AMD.(4-6)

Besides of being one of the first substances to be used in PRBs for groundwater remediation, *zero-valent iron*, ZVI, shows a larger capacity than conventional compounds for the sequestration of metal ions from water.(7,8)

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 tetrahydridoborate) – an inorganic compound with the formula $NaBH_4$. Zero-valent iron is prepared *via* reduction of *ferric* iron by adding to an aqueous solution of $FeCl_3{\cdot}6H_2O$ an aqueous solution of $NaBH_4$.

Aim of this work is to study the fundamentals of sodium borohydride *hydrolisis* for the synthesis of ZVI from iron chloride aqueous solutions, and the *immobilization* (reduction) of metal ions with zero-valent iron. All 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 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 $NaBO_2$ and gaseous hydrogen as products.

The conversion of hydrogen from *water* into hydrogen *gas* is of such importance that this substance is taken into high consideration when it comes to the production and storage of hydrogen for generating electricity through fuel cells. In such case the term ‘steam hydrolysis’[1] is used:

$NaBH_4 + 2\ H_2O(g) = 4\ H_2(g) + NaBO_2$ (1)

Ideally, 2 moles of water are required to liberate 4 moles of gaseous hydrogen, but in practice excess water is required because the solid by-product can exist with varying degrees of hydration (*i.e.* hydrated metaborates); the term x accounts for excess water in Eq. (2).(9)

$NaBH_4 + (2 + x)\ H_2O = 4\ H_2(g) + NaBO_2 \cdot x\ H_2O$ (2)

It is known since the middle of the 20th century(10) 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 $NaBH_4$ in this work lies on this particular aspect. In order to promote the reduction of aqueous ferric and ferrous ions into zero-valent iron, ZVI, it becomes necessary to add a strong reducing agent to the water. Further, the iron produced by this method tends to come out in the form of fine-grained loose particles – often nano-sized – which is very important to the intended use.

Added to water, $NaBH_4$ undergoes hydrolysis (also called *self-hydrolysis* to differentiate it from hydrolysis in the presence of a catalyst), usually represented by some stoichiometric reactions:(11-13)

$NaBH_4 + 2\ H_2O = 4\ H_2(g) + NaBO_2(aq)$

$NaBH_4 + 4\ H_2O = 4\ H_2(g) + NaOH + H_3BO_3$

$NaBH_4 + 4\ H_2O = 4\ H_2(g) + NaB(OH)_4(aq)$

The reaction mechanism is multifaceted and pH-dependent. As the formed byproduct is basic, pH rises and the reaction slows.

2.2 Electroless Deposition of Iron

To explain the reduction of iron ions, some stoichiometric reactions are referred to in the literature:(14-16)

$Fe^{2+} + 2\ BH_4^- + 6\ H_2O = Fe^{o} + 2\ B(OH)_3 + 7\ H_2$

$Fe^{3+} + 3\ BH_4^- + 9\ H_2O = Fe^{o} + 3\ H_2BO_3^- + 12\ H^+ + 6\ H_2$

$Fe(H_2O)_6^{3+} + 3\ BH_4^- + 3\ H_2O = Fe^{o} + 3\ B(OH)_3 + 10.5\ H_2$

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 4500 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 the other FACT databases.

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[1] The United States Department of Energy (DOE) made a “no-go” decision in 2007 on the viability of *aqueous* $NaBH_4$ 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* $NaBH_4$ and steam.

Despite the use of the term ‘compound’ in this database, two solutions are represented: the gas and the aqueous phases.

Boron containing *ions* and *aqueous compounds* from both databases used in the present work can be seen in Table 1.

Table 1: Aqueous species containing boron, present in FACT53 database

FACT53	BH_4[-], BO_2[-], B_4O_7[2-], H_2BO_3[-], $H_2BO_3(H_2O_2)$[-], HB_4O_7[-], $H_5(BO_3)_2(H_2O_2)_2$[-], $H_2B_4O_7$(aq), H_3BO_3(aq)

3.2 Experiments

The experiments include: production of ZVI and precipitation of metal ions from water (immobilization).

All chemicals used were *reagent grade* and water was de-ionized.

$NaBH_4$ (Vetec) and $FeCl_3{\cdot}6H_20$ (Vetec) were used to prepare ZVI. The synthesized iron was used in metal ion sequestration experiments.

Metal salts to emulate AMD solution include $CuSO_4{\cdot}5H_2O$ (Labsynth), $NiSO_4{\cdot}6H_2O$ (Labsynth) and $Al_2(SO_4)_3{\cdot}(14\text{-}18)H_2O$ (Vetec).

4 RESULTS AND DISCUSSION

4.1 $NaBH_4$ Hydrolysis

The dissolution of $NaBH_4$ in water was simulated using FACT53 database for a sodium borohydride amount ranging from $1x10^{-6}$ to 1 [g] for each liter of water.

The simulation results can be seen in Figure 1. Of all species containing boron in the FACT53 database (see methodology), only three have significance. BO_2^- is the most abundant of them in the higher end of the amount range while H_3BO_3(aq) takes this position on the other extreme of NBH_4 amount range.

4.2 Stoichiometric Reactions

Using FACT53 database, the simplest reaction which can be written is:

$NaBH_4 + 2\ H_2O = 4\ H_2(g) + Na^+ + BO_2^-$

In order to take into account the production of the $H_2BO_3^-$ ion and H_3BO_3(aq), a new decomposition stoichiometric reaction was written:

$2\ NaBH_4 + 7\ H_2O = 8\ H_2(g) + 2\ Na^+ + H_2BO_3^- + H_3BO_3(aq) + OH^-$

overall reaction, then, becomes:

$3\ NaBH_4 + 9\ H_2O = 12\ H_2(g) + 3\ Na^+ + H_2BO_3^- + H_3BO_3(aq) + OH^- + BO_2^-$

The logarithm of the equilibrium constant for this stoichiometric reaction, at 298.15 [K], is iqual to +172.5. This simply means that sodium borohydride is highly unstable in the presence of water.

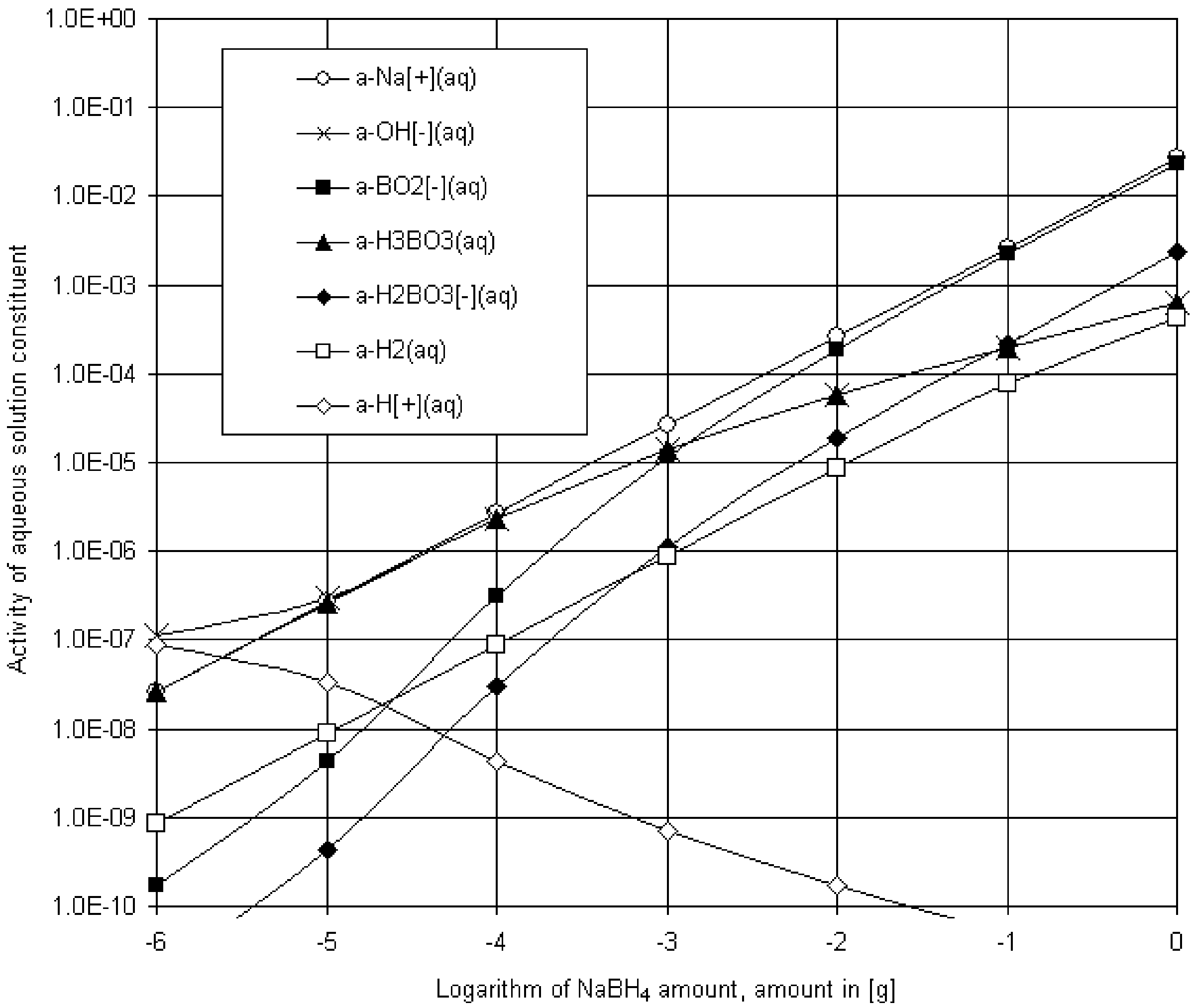

Figure 1. Activity of aqueous solution constituents as a function of the logarithm of $NaBH_4$ amount added to 1 [L] water (FactSage).

4.3 Pourbaix Diagram

Overlaying the electrochemical potential as a function of pH for each amount of $NaBH_4$ added to 1 [L] water on the Pourbaix diagram for iron it is possible to see the strong reducing effect of sodium borohydride addition on the water (Figure 2).

Chances are, that Feº is the only *solid* phase in the equilibrium state. This, certainly, relies only on kinetics aspects – once thermodynamics predicts the presence of the stable phase $Fe(OH)_2(s)$. Hydroxides (or oxides) are composed of *more* than one kind of atom and this fact may play an important role in the crystallization process, delaying the precipitation of these solids.

To cope with this fact, the solid iron oxides and hydroxides were withdrawn from the databases. Therefore, metastable iron (ZVI) is able to precipitate at *loci* on Pourbaix diagram where Fe_3O_4 or $Fe(OH)_2$ are stable phases. This information must be kept in mind when reading the results from the simulation of the electroless deposition of iron (this situation was *reversed* before the simulation of the sequestration of metal cations from AMD).

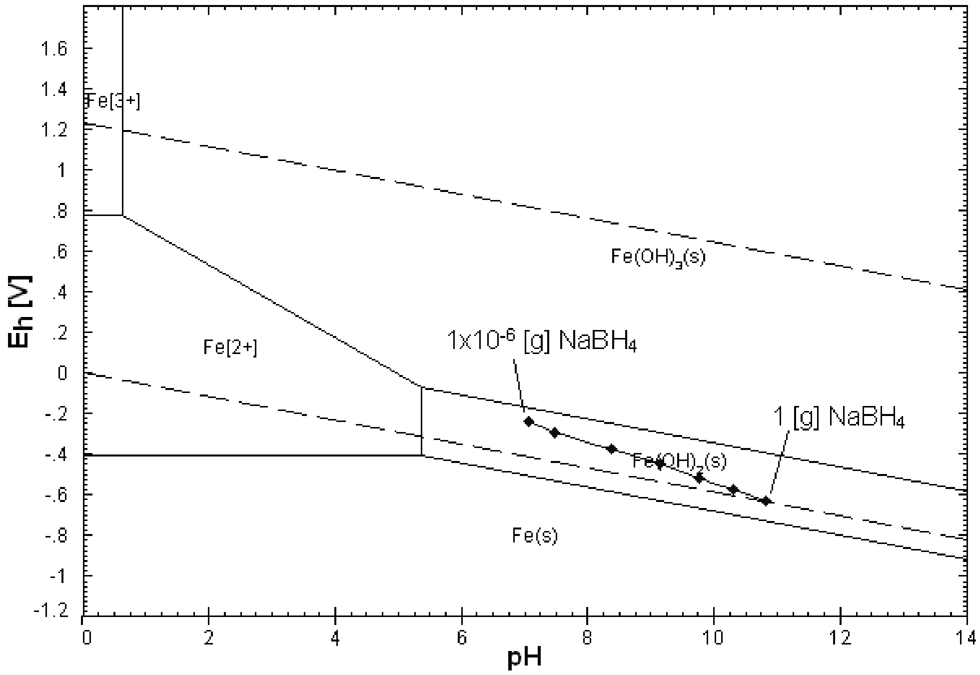

Figure 2. Electrochemical potential as a function of pH for selected amounts of $NaBH_4$ added to 1 [L] water overlaying the Pourbaix diagram for iron (FactSage)

To cope with this fact, the solid iron oxides and hydroxides were withdrawn from the databases. Therefore, metastable iron (ZVI) is able to precipitate at *loci* on Pourbaix diagram where Fe_3O_4 or $Fe(OH)_2$ are stable phases. This information must be kept in mind when reading the results from the simulation of the electroless deposition of iron (this situation was *reversed* before the simulation of the sequestration of metal cations from AMD).

4.4 Electroless Deposition of Iron

The electroless reduction of iron ions was simulated using a simple scheme: a certain amount of solid $NaBH_4$ is added to a plain solution of Fe and Cl ions in water.

Adding sodium borohydride to ferric chloride and ferrous chloride aqueous solutions containing each 0.005 [mole] of reactant produces different effects. When the amount of $NaBH_4$ added to the water is *small*, the ratio Cl/Fe is of importance: for a high Cl/Fe ratio (use of reactant $FeCl_3$), chloride ions tend to stabilize the iron ions in solution, causing *no* ZVI precipitation. This effect lessens for higher $NaBH_4$ amounts, Table 2.

Table 2. Percentage of ZVI (mass basis, Fe total mass is 0.273 [g]) for two amounts of $NaBH_4$ added on a solution containing 0.005 [mole] $FeCl_2$ (or $FeCl_3$) in 1 [L] water (FactSage)

Amount of $NaBH_4$	1 [g]	10 [g]
with $FeCl_2$	21.1	94.2
with $FeCl_3$	0.0	91.4

Interesting to note, iron ions reduction by BH_4^- – as it is cited in the literature (see above) – is not confirmed by the simulations, since its activity is very small, allways $< 1x10^{-50}$, even after adding 10 [g] of $NaBH_4$ on water.

4.5 Immobilization of Metals

The experimental efficacy 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 those metals were used: $CuSO_4$, $NiSO_4$ and $Al_2(SO_4)_3$. Based on knowledge of AMD composition, three concentrations were chosen: 50, 200 and 130 [mg/L], respectively. Later these values were adjusted to 54, 217 and 132 [mg/L] in order to reproduce the values used experimentally.

Results show that thermodynamics predicts the *total* removal of Cu, Ni and Al cations from AMD (Table 3).

Table 3. Percentage of metal precipitated (mass basis) after (and before) the addition of 2 [g] ZVI on a solution containing cations of Cu, Ni and Al; experimental content remaining in solution after treatment are given for two elapsed time periods

Metal	Initial amount [mg/L]	Percentage precipitated [wt.%] and phase (Thermodynamic *simulation*) (FactSage)				Content remaining in solution [mg/L] (*Experiment*) Time elapsed	
		Before*	Phase**	After*	Phase**	5 [min]	5 [day]
Cu	54	*1.3*	$Cu(OH)_2(s)$	*100*	$Cu_5FeS_4(s3)$	0.02	0.02
Ni	217	*0.0*	$Ni_3S_2(s)$	*100*	$Ni_3S_2(s)$	170	5
Al	132	*12.7*	$Al_2O_3(H_2O)(s)$	*100*	$Al_2O_3(H_2O)(s)$	105	13

** Before and after addition of 2 [g] ZVI* *** As described in FACT53 database*

As it can be seen, precipitates resulting from simulated treatment of solutions with 2 [g/L] sodium borohydride are complex and simple sulfides and hydroxides – depending on the metal – and reproduce fairly well the experimental results after 5 days of contact time.

5 CONCLUSIONS

A new stoichiometric reaction for sodium borohydrate hydrolysis was written:

$$3\ NaBH_4 + 9\ H_2O = 12\ H_2(g) + 3\ Na^+ + H_2BO_3^- + H_3BO_3(aq) + OH^- + BO_2^-$$

The importance of BH_4^- ion – frequently cited in the literature – was not confirmed by the simulations, since its activity is always very small.

The addition of sodium borohydride on water produces simultaneously a pH increase and a redox potential decrease, with increasingly $NaBH_4$ amounts, that leads to the required conditions for the reduction of ferric or ferrous iron ions (production of zero-valent iron, ZVI) from aqueous chloride solutions.

As it was 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 extractive metallurgical process. The cementation process, however, produces *metallic* copper, which is *not* thermodynamically stable in water. Consequently, a copper-iron sulfide is obtained, instead, with 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 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 stable – thermodynamics predicts that *alumina monohydrate precipitates even without iron addition*, see Table 3. Yet, for a reason not known up to now, all Al will precipitate as *diaspore* when ZVI is added to the solution.

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