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EXPERIMENTAL AND COMPUTATIONAL ANALYSIS FOR THE ASSESSMENT OF THE INFLUENCE OF IRON NANOPARTICLES MASS ON THE SEQUESTRATION OF METALLIC AQUEOUS IONS

M. A. Liendo[1], N. C. Heck[2], G. E. Englert[1], C. H. Sampaio [1]

[1] Lab. de Processamento Mineral, LAPROM – Mining Eng. Dept. – Universidade Federal do Rio Grande do Sul, UFRGS, Campus do Vale – Av. Bento Gonçalves 9500
91501-970 Porto Alegre – RS – BRAZIL, Telephone: (55-51) 3308-7103 – Fax: (55-51) 3308-7116 – e-mail: liendo_alejandra@yahoo.com
[2] Núcleo de Termod. Comput. para a Metalurgia, NTCm – Metall. Eng. Dept. – Universidade Federal do Rio Grande do Sul, UFRGS, Campus do Vale – Av. Bento Gonçalves 9500
91501-970 Porto Alegre – RS – BRAZIL, Telephone: (55-51) 3308-7102 – Fax: (55-51) 3308-7116 – e-mail: heck@ufrgs.br

ABSTRACT – Acid mine drainage (AMD) is the process resulting from acid water generation due to simultaneous effect of oxygen and atmospheric humidity on sulfide minerals. Permeable reactive barriers (PRBs) have being developed in the last years as an alternative to the treatment of groundwater contaminated by AMD. The aim of this work is to evaluate an alternative methodology for sequestrating of Al, Cu and Ni involving nanoparticles of iron as reactive material in PRBs. A computational study was carried out, simulating the thermodynamics of the focused phenomena. For this study, the Canadian-German group CRCT/GTT's FactSage v.5.5 software was used. The effects of the mass iron particles added to the solution containing metallic ions have also been explored. Preliminary results, experimental and computational, show an elevation in the value of pH and a concentration reduction of metallic ions as contact time and mass increases.

KEY WORDS: nanoparticles of iron; factsage; sequestration of metals

RESUMO – A drenagem ácida de minas (DAM) é o processo que gera águas ácidas devido ao efeito simultâneo do oxigênio e da umidade atmosférica em minerais sulfetados. Barreiras permeáveis reativas (BPRs) têm sido desenvolvidas nos últimos anos como alternativa para o tratamento de águas subterrâneas contaminadas com DAM. O objetivo deste trabalho é avaliar uma metodologia para o seqüestro de Al, Cu e Ni envolvendo nanopartículas de ferro como material reativo em BPRs. Um estudo computacional termodinâmico foi realizado, simulando o fenômeno estudado. Para este estudo, o software do grupo Canadense-Alemão, CRCT/GTT FactSage v.5.5 foi usado. O efeito da massa das nanopartículas de ferro adicionadas à solução contendo íons metálicos também foi explorado. Os resultados preliminares experimentais e computacionais obtidos mostraram uma elevação no pH e redução na concentração dos íons metálicos com a massa e o tempo de contato.

PALAVRAS-CHAVE: nanopartículas de ferro; FactSage; seqüestro de metais.

1. INTRODUCTION

Acidic sulfur-rich wastewaters are known by-products of industrial operations such as galvanic processing and scrubbing of flue gases at power plants. The major producer of such effluents is, however, the mining industry. Water draining from active and, in particular, abandoned mines and mine wastes are often acidic therefore the name of Acid Mine Drainage (AMD). The production of AMD usually – but not exclusively – occurs when sulfide-bearing material is exposed to oxygen and water (Alkcil and Koldas, 2005). Because mineralogy and other factors affecting AMD formation are highly variable, composition changes from site to site. Such waters represent a risk to the environment for the reason that they often contain elevated concentrations of metals and metalloids (Jonhson and Hallberg, 2005) and can contaminate surface and groundwater, as well as soils.

Permeable Reactive Barriers (PRBs) have been developed and used to treat groundwater contaminated by inorganic constituents. They must be placed in the path of a migration plume of contaminated groundwater. Reactive materials within the barrier are selected to promote geochemical reactions for destruction or stabilization of the groundwater contaminants. Ideally, these materials are sufficiently reactive to treat water for periods of years or decades (Blowes *et al.*, 2003).

Southern Brazil is known for the occurrence and utilization of coal in several industries and in energy generation. The largest Brazilian coal reserve is found in the Rio Grande do Sul-State (RS) and accounts for 60% of the total. On the other side, the area of occupation of residues of coal requires an evaluation of the influence of such material in the contamination of groundwater. In view of the increasing degradation of surface water resources, the possibility of utilization of aquifers as drinking water supplies is of great importance. Hence, problems related to the groundwater contamination in areas which can influence aquifers are of great concern (Binotto *et al.*, 2000).

Permeable reactive barriers of *zero-valent iron* (ZVI) have proven to be a promising technology for the remediation of groundwater for several compounds (Fukurawa, 2002); (Blowes *et al.*, 2003), (Cantrell *et al.*, 1995); (Puls *et al.*, 1999). The results obtained by some researchers showed that ZVI is effective in rapidly neutralizing acid and promoting removal and immobilization of dissolved heavy metals (Shokes and Möller, 1999), (Shelp *et al.*, 1995), (Wilkin and McNeil., 2003).

On the other hand, nanoscale inorganic particles and their agglomerates offer excellent opportunities for selective removal of a variety of target compounds from contaminated water bodies, for example elemental iron (Cumbal *et al.,*2003). Nanoscale iron particles represent a new generation of environmental remediation technologies that could provide cost-effective solution to some of the most challenging environmental cleanup problems. Nanoscale iron particles have a large surface areas and high surface reactivity. Equally important, they provide enormous flexibility for *in situ* applications. (Zhang 2000)

In this investigation, Nanoscale iron particles have been evaluated, both experimentally and theoretically, for increasing pH value and metals sequestration from aqueous solutions in batch studies.

2. METHODOLOGY

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2.1 Thermodynamic simulations

Experimental behavior has been evaluated against a theoretical analysis done with the help of chemical thermodynamic simulations.

The software employed for the thermochemical simulations was the FactSage (version 5.5) software, described in the literature (Bale *et al*., 2002). This software includes the Equilib module, which is the Gibbs energy minimization workhorse of FactSage. It calculates the amount and concentration of chemical species at the state of equilibrium from elements or compounds in conjunction with finite values for some state variables selected as input.

The FACT53 database (FS53Base.cdb), released in January 2007, which contains thermodynamic data for over 4500 compounds (pure substances as well as aqueous and gas ions) was utilized together with the FactSage software.

It must be pointed out, nevertheless, all the considerations presented in this investigation are limited to the equilibrium aspects of the systems, in spite of the recognition that kinetic aspects may be equally important. The thermodynamic approach does, however, establish the direction of the reactions and the limiting conditions.

In real water bodies, concerning thermochemical simulations, two major conditions can be distinguished: one where oxygen is abundant and another where there is an oxygen deficit. In this investigation, *only* the *last* condition was explored – that is, *no* oxygen was added. This condition was chosen making an allowance for the credible *reducing conditions* existing locally.

Iron was used, as a calculation input, in the following proportions 0.1, 0.2, 0.3, 1 and 3 g/L. Since no kinetic resistances of any kind are taken into consideration in a thermodynamic analysis, all the iron added into the system *will* react – unless the thermodynamic equilibrium is reached before. Hence, there is *no* similarity with the amounts of Fe which are actually added to the solution in real experiments.

Only Al, Ni and Cu metals were taken into consideration. For cooper, two kinds of simulations where done: *unrestricted* and *restricted*; by the last one it is meant a simulation where only metallic iron and cooper exist in the equilibrium state as solid products.

Temperature and system pressure were set to 25ºC and 1 atm for all determinations.

2.2 Chemicals used

All chemicals were reagent grade and water was de-ionized. Metal salts include $CuSO_4 \cdot 5H_2O$ (Labsynth), $NiSO_4 \cdot 6H_2O$ (Labsynth) and $Al_2(SO_4) \cdot (14-18) \ H_2O$ (Vetec). For cleaning, de-ionized water, HNO_3 65% (Quimex) and Ethanol (Vetec). Synthesized iron was used for batch experiments. $NaBH_4$ (Vetec) and $Cl_3Fe \cdot 6H_2O$ (Vetec) were used to prepare synthesized iron.

3. RESULTS AND DISCUSSION

3.1 Simulations

From the thermodynamic point of view, ZVI has proven effective in promoting removal and immobilization of Cu, Al and Ni aqueous ions, since no metal ion remained in solution after the addition of any of the selected mass values (0.1 to 3 g Fe).

Equilibrium E_h and pH values, for Al, Ni and Cu metal ions solutions, as function of iron

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additions, can be seen in Figure 1. Clearly, an increase in the pH values is the main characteristic of the simulated results, but also the depletion of oxygen from the solution – as it can be seen from the tendency for equilibrium values to cross the pH_2 (at 1 atm) line –, with greater iron amounts, is worth to notice. Cu, under *restricted* conditions shows, a stronger this tendency, but the general behavior remains the same.
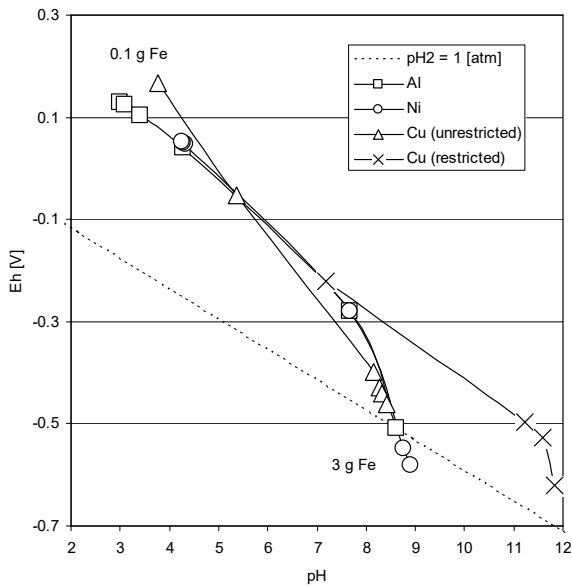

Figure 1 – Equilibrium Eh and pH values as function of Fe additions (0.1 to 3 g) for Al, Cu and Ni aqueous ions

Table 1 – Mass (g) of precipitates obtained when ZVI is added to an aqueous solution containing 80 ppm Cu ions

ZVI (g/L)	0.1	0.2	0.3	0.6	1	3
(Cu2O)(Fe2O3)(s2)	**0.062**					
Cu2S_chalcocite(s)	**0.067**					
FeS2_pyrite(s)		0.011				
Fe2O3_hematite(s)	0.052	0.254				
CuFeS2(s)			**0.038**	**0.038**		
Fe3O4_magnetite(s)			0.382	0.797	1.343	4.107
FeS(s)					0.022	0.022
Cu5FeS4(s3)		**0.126**	**0.105**	**0.105**	**0.126**	**0.126**

Under low oxygen conditions levels and high mass of Fe, several compounds precipitate, Tables 1 to 3.

The interaction of copper with iron is relatively notorious, since the *cementation* of aqueous copper ions with iron (*scrap*) is an extractive metallurgical process. The cementation process produces *metallic* copper, which is *not* thermodynamically stable in water under the experimental conditions. This, however, follows Ostwald's rule, which says that if the crystal phase is stable, however it *never* appears, another meta-stable phase forms.

Water saturates with iron before 0.6 g Fe is added to the solution, but all the copper is already *cemented* by 0.1 g Fe. Under *unrestricted* conditions, however, the phases precipitated are solid oxides and sulfur compounds, Table 1.

Table 2 – Mass (g) of precipitates obtained when ZVI is added to an aqueous solution containing 200 ppm Ni ions

ZVI (g/L)	0.1	0.2	0.3	0.6	1	3
NiSO4(H2O)7_morenosit(s)	**0.653**	**0.355**	**0.037**			
(NiO)(Fe2O3)(s2)	**0.136**	**0.307**	**0.463**			
Ni3S4_ni3s4_polydymit(s)		**0.099**	**0.142**			
NiS2(s)			**0.006**			
FeS2_pyrite(s)				0.024		
Ni9S8_ni9s8(s)	**0.056**		**0.310**			
Fe2O3_hematite(s)				0.074		
Fe3O4_magnetite(s)				0.742	1.290	4.054
FeS(s)					0.104	0.104
Ni3S2(s)					**0.285**	**0.285**

Nickel, with the standard electrode reduction potential of -0,25 V, is slightly more noble than iron, with -0.44 V, but cementation of nickel ions is effective only if the electromotive force is high, as with a much more reactive metal, like Zn. The removal of Ni, therefore, is accomplished by precipitation of several nickel sulfate, sulfide and oxide compounds, Table 2.

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Table 3 – Mass (g) of precipitates obtained when ZVI is added to an aqueous solution containing 120 ppm Al ions

ZVI (g/L)	0.1	0.2	0.3	0.6	1	3
Al2O3(H2O)_diaspore(s)	**0.116**	**0.190**	**0.258**	**0.266**	**0.266**	**0.266**
FeS2_pyrite(s)	0.031	0.061	0.092	0.236	0.400	
FeSO4(H2O)7_melant.it(s)			0.085			
Fe2O3_hematite(s)				0.486	0.266	
Fe3O4_magnetite(s)					0.868	3.631
FeS(s)						0.586

For aluminum, a metallic product is impossible. This was naturally expected, due to the known great reactivity shown by this metal. Apart from diaspore – the only compound bearing Al –, *precipitates* are oxides, sulfate and sulfides of iron, Table 3.

3.2 Experiments

The modification in Al concentration as a function of the amount of iron and time is shown in Figure 2. Lines *t1* and *t2* represent (for *all* Figures) the contact times of 5 min and 5 days, respectively.
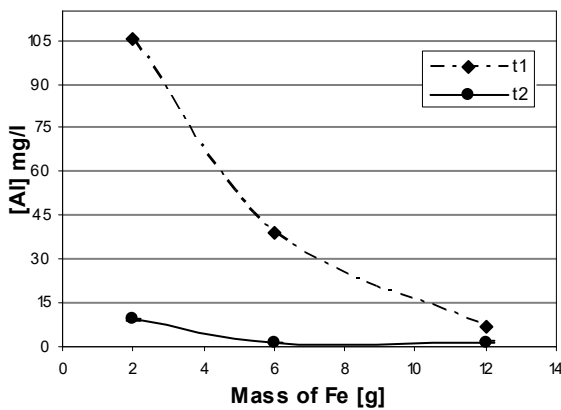

Figure 2 – Evolution of Al concentration with time as a function of iron mass; initial concentration was 132 mg/L

The behavior of E_h and pH with iron additions is shown in Figure 3. As can be seen, there is an increase in pH values with the increasing amount of iron, while E_h shows a

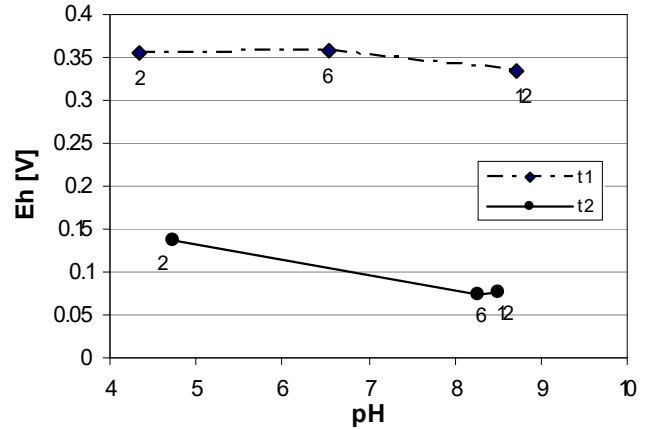trend to change to more reductive conditions with time only.

Figure 3 – Behavior of Eh-pH for Al solutions as a function of time and Fe amount; numbers indicate the iron amount; initial pH = 3.79

For Cu, concentration has a rapid and significant decrease. So time and iron amount do not play a key role, Figure 4.
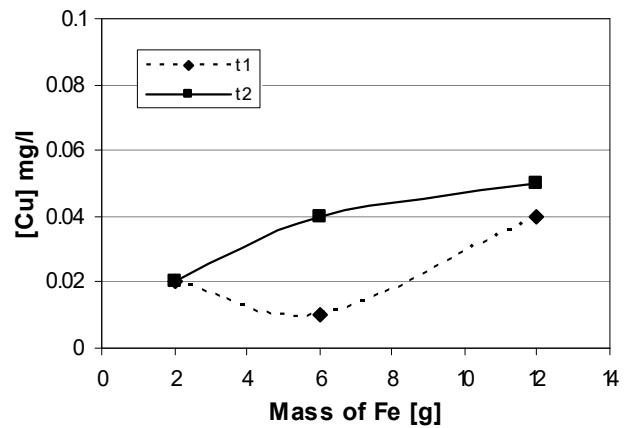

Figure 4 – Evolution of Cu concentration with time as a function of iron mass; initial concentration was 54 mg/L

Changes in E_h and pH for Cu solution with time and iron amount are shown in Figure 5. The E_h value decreased with time, although it

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seems that a change in E_h or pH is not significantly dependent from the iron mass.
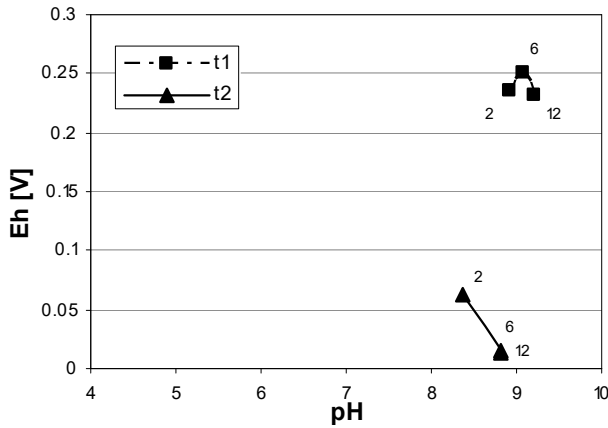

Figure 5 – Behavior of Eh-pH for Cu solutions as a function of time and Fe amount; numbers indicate the iron amount; initial pH = 4.93

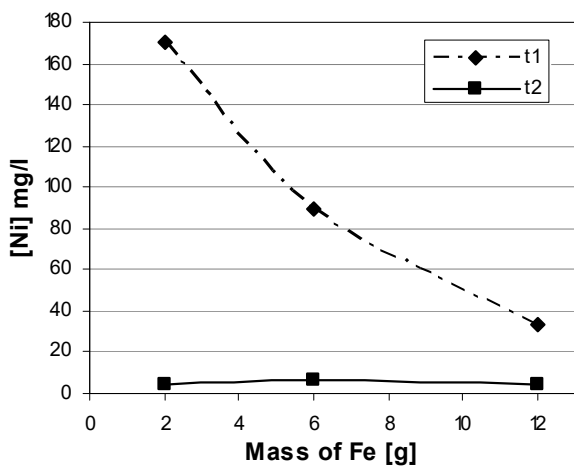Ni concentration dependence with time and iron mass is shown in Figure 6.

Figure 6 – Evolution of Al concentration with time as a function of iron mass; initial concentration was 217 mg/L

The Ni concentration decreases with the iron mass (for *t1*). For different iron amounts, it

varies from 85 to 22 per cent of the initial Ni content.

Inspection of Figure 7 shows that E_h and pH changes are somewhat similar to those from solutions containing Cu.
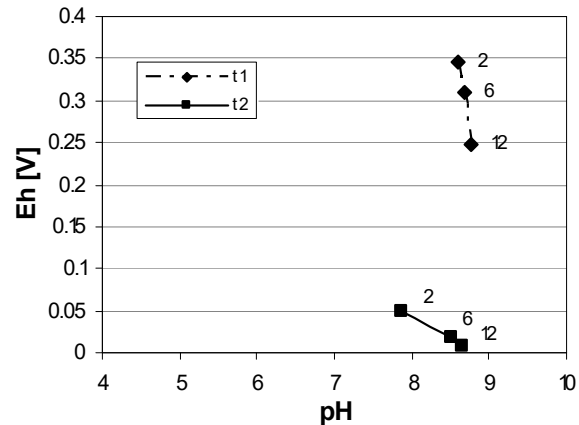

Figure 7 – Behavior of Eh-pH for Ni solutions as a function of time and Fe amount; numbers indicate the iron amount; initial pH = 5.42

4. CONCLUSIONS

It can be shown, from experimental and theoretical results, that ZVI nanoparticles can promote immobilization of dissolved Al, Cu and Ni metal ions. pH increased and redox potential decreased with time (experimentally) and increasing iron amounts.

From the thermodynamic simulations it can be seen that precipitates range from complex to simple oxides, sulfates and sulfides, depending on the amount of iron added to the system.

From a comparison of the present experimental study with previous work done with commercial iron, it seems that the precipitation is faster when zero-valent iron nanoparticles are used.

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