

## A SIMPLE METHOD TO SELECT ZEROVALENT IRON MATERIALS FOR GROUNDWATER REMEDIATION

Dr. Chicgoua Noubactep, Centre of Geosciences - Applied Geology; University of Göttingen; Germany

Dr. Mamadou Fall, Université du Québec en Abitibi-Témiscamingue (UQAT), Rouyn-Noranda, Canada

PD Dr. rer. nat. habil. Günther Meinrath, RER Consultants, Passau, Germany

Prof. Dr. Broder Merkel, Technical University Bergakademie Freiberg, Institute of Geology, Freiberg, Germany.

### ABSTRACT:

The iron dissolution in a diluted EDTA-solution (2 mM) has been investigated for thirteen zerovalent iron (ZVI) materials (mild steel and cast iron). It has been found out that the reactivity of a ZVI in a 2 mM EDTA solution is a linear function of the time for the first 72 hours. The dissolution rate can help to characterize the reactivity of the individual materials under natural near conditions and to quantify the amount of corrosion products on the material. The efficiency of the proposed method was validated by comparing the obtained results to that of uranium fixation by the same materials. The EDTA-method can generally be used as a powerful screening test for the selection of ZVI materials. The method is very cheap and has the double advantage of not requiring any special equipment nor dangerous chemicals.

### RÉSUMÉ:

Une méthode de comparaison des matériaux en fer métallique ( $\text{Fe}^0$ ) en vue d'une utilisation dans la dépollution in situ des eaux souterraines a été mise sur pieds. La méthode consiste à caractériser la dissolution par complexation des matériaux dans une solution diluée d'un sel disodique de l'EDTA (2 mM). Il a été montré que la dissolution du fer métallique dans cette solution d'EDTA est une fonction linéaire du temps pendant les trois premiers jours de l'expérience. La pente de la droite représente la vitesse de dissolution et est caractéristique pour chaque matériau pendant que l'ordonnée à l'origine permet une quantification du volume des produits de corrosion présent sur le matériau initial. La comparaison des résultats de la méthode EDTA avec ceux de la fixation de l'uranium par les mêmes matériaux (13 au total) valide la méthode qui peut être utilisée de manière général pour une sélection rapide des matériaux. La méthode EDTA présente par ailleurs le double avantage de son faible coût de de l'extrême simplicité de son mode opération.

### 1. Introduction

The use of zerovalent Iron (ZVI;  $\text{Fe}^0$ ) for in situ groundwater remediation purposes is currently under investigation (Naftz et al. 2002, Phillips et al. 2003). It has been first developed for chlorinated solvents and efforts are made to extend and optimize their application for a large pallet of contaminants (Gillham & O'Hannesin 1994, Matheson & Tratnyek 1994, Powell et al. 1995, Blowes et al. 2000).

The decontamination process is based on iron dissolution from ZVI materials, known as aqueous corrosion. Although the new technology consist in "putting corrosion to use" (Tratnyek 1996), only few results from the corrosion science of iron and steel are helpful for the new application (Noubactep et al. 2004). For example, the intrinsic factors that affect the corrodibility of mild steels and cast irons have

not been clearly identified (Piwowarsky 1951, Klas & Steinrath 1974, Briehl 1995, Mercer & Lumbard 1995, Tostmann 2001). Furthermore, cast irons are the most used materials for subsurface pipes, although they exhibit a greater corrodibility than mild steels due to the larger heterogeneity of their crystal structure (Piwowarsky 1951, Klas & Steinrath 1974). On the other side, laboratory tests for corrosion characterization are all more or less far from the natural conditions since they all consist in attacking metallic materials with aggressive agents (Evans 1939, Piwowarsky 1951). These tests are also expensive and to some extend complicated. At present, there are no routine procedures for testing and selecting  $\text{Fe}^0$  materials for subsurface applications. Therefore applicable methods are needed, that could accurately test  $\text{Fe}^0$  materials for groundwater remediation.

**Table 1:** Some relevant reactions for the discussion of the behaviour of the iron material under the experimental conditions of this work.

Process	Reaction	Eq.
Iron dissolution	$\text{Fe}^0 \Rightarrow \text{Fe}^{2+} + 2 \text{e}^-$	[1]
Iron dissolution	$\text{Fe}^0 + \text{EDTA} \Rightarrow \text{FeEDTA}^{2+} + 2 \text{e}^-$	[2]
FeOOH dissolution	$\text{FeOOH} + \text{EDTA} + 3 \text{H}^+ \Rightarrow \text{FeEDTA}^{3+} + 2 \text{H}_2\text{O}$	[3]
$\text{Fe}^{2+}$ oxidation	$2 \text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \Rightarrow 2 \text{Fe}^{3+} + 2 \text{OH}^-$	[4]
$\text{Fe}^{2+}$ complexation	$\text{Fe}^{2+} + \text{EDTA} \Rightarrow \text{FeEDTA}^{2+}$	[5]
$\text{Fe}^{3+}$ complexation	$\text{Fe}^{3+} + \text{EDTA} \Rightarrow \text{FeEDTA}^{3+}$	[6]

Before the implementation of any Fe<sup>o</sup> material in an application, it has to be tested for its ability to remove the targeted contaminant. The current approach consists in testing available materials for their removal efficiency mostly for one contaminant and selecting the one showing the best removal goal (e.g. Powell et al. 1995, Rodenhäuser 2003, Tamara & Butler 2004). This purpose is complicated by two key factors that have been found to influence the interaction of Fe<sup>o</sup> materials with the contaminant: the oxidation state of the iron surface and the presence of atmospheric corrosion products on it (Powell et al. 1995, Noubactep et al. 2001). The material post reactivity over this initial phase is yet to be properly addressed (Noubactep et al. 2004).

This work was undertaken to elaborate a simple and cheap technique to select Fe<sup>o</sup> materials for any application. For this purpose thirteen Fe<sup>o</sup> materials were rationally selected and tested for their iron dissolution in a diluted solution of ethylenediaminetetraacetic (EDTA, 2 mM). Particular attention was directed at determining the extent to which the presence of corrosion products on the surface affects the iron production of Fe<sup>o</sup> materials.

## 2. Theoretical Background

Metal ions are strongly complexed by synthetic anthropogenic chelating agents such as EDTA at neutral pH. This process is currently used in studying the remobilization of metals, mostly from iron and manganese oxides (e.g. Nowack et al. 1996). In these processes, metal ions are released back into solution mostly through oxides dissolution by chelating agents (Eq. 3, Tab. 1). The use of EDTA in geochemical investigations has especially been addressed because of their potential for increasing the solubilization and remobilization of heavy metals from aquatic sediments or from aquifer material during the infiltration from river water to groundwater (Hering & Morel 1990).

In investigating the mechanism of contaminant uptake by ZVI materials, EDTA have been used for two different purposes: (1) Abdelouas et al. (1999) used EDTA to avoid the formation of corrosion products, and therefore eliminating adsorption as possible uptake mechanism and (2) Noubactep et al. (2004) used EDTA (100 mM) as aggressive agent to accelerate corrosion and possibly address the reactivity of ZVI materials over the initial phase of the barrier implementation.

In this study EDTA (2 mM) is used as mild dissolution agent for Fe<sup>o</sup> materials (and corrosion products). Table 1 summarises some relevant reactions for the discussion under the experimental conditions of this work. The primary aqueous iron corrosion (iron dissolution, Eq. 1) is expected

to be enhanced and accelerated in the presence of EDTA (Eq. 2). If the initial iron material is rusted, then the corrosion products (e.g. FeOOH) will be dissolved by a complexation reaction (Eq. 3). Fe<sup>2+</sup> from Eq. 1 (or FeEDTA<sup>2+</sup> from Eq. 2) will be oxidized by air oxygen to Fe<sup>3+</sup> (Eq. 4). Finally Fe<sup>2+</sup> and Fe<sup>3+</sup> from Eq. 1 and Eq. 4 will be complexed by EDTA (Eq. 5 & 6).

Corrosion products are usually mixture of iron oxides (FeOOH, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>) and it is expected, that the kinetics of their EDTA dissolution will primarily depend on the crystallinity of the oxide. The kinetics of the EDTA dissolution of ZVI on the other side will primarily depend on: (1) the roughness and the porosity of the surface, and (2) the oxidation state of the surface (presence of rust). Other factors such as crystallinity, iron impurity, morphology or the impact of thermal treatment by the material manufacture can not be appropriately discussed neither with this approach nor with current testing methods (Noubactep et al. 2004).

The basic idea of this approach is to exploit the differential dissolution behaviour of Fe<sup>o</sup> materials in a 2 mM EDTA solution to characterise their suitability for subsurface applications. At any datum (t) after the start of the dissolution experiment (t<sub>0</sub>), the total iron concentration ([Fe]<sub>t</sub>) as defined in Eq. 7 can be described as a function of time. It is expected, that for a certain time frame after t<sub>0</sub>, the total aqueous iron concentration (Eq. 7) will be a linear function of the time (Eq. 8).

$$[\text{Fe}]_t = [\text{Fe}^{2+}] + [\text{Fe}^{3+}] + [\text{FeEDTA}^{2+}] + [\text{FeEDTA}^{3+}] \quad [7]$$

$$[\text{Fe}]_t = a \cdot t + b \quad [8]$$

Therefore, this study targeted at identifying the time frame for which the linearity of Eq. 8 is assured. If this is done, then the regression coefficients “a” and “b” in Eq. 8 can be used to characterise the individual materials. In fact, “a” can be defined as the rate of Fe dissolution (from Fe<sup>o</sup> or oxides) whereas “b”, the iron concentration at t<sub>0</sub> (ideally zero; b = [Fe]<sub>t0</sub>), can give an estimation of the amount of corrosion products on the material. In fact, if parallel experiments are conducted with not treated and pre-washed iron materials (freeing the surface from rust), then the difference of the b-values will give an estimation of the amount of available corrosion products. By pre-washing the same material with solutions of different aggressive capacities (e.g. 0.25 M HCl) it is expected that indications about the reactivity of the individual materials can be obtained.

**Table 2.** Elemental composition of iron materials used in this study.

ZVI	elemental composition (%)								
	C	Si	Mn	P	S	Cr	Mo	Ni	Fe
<b>C15</b>	0.12	0.26	0.62	0.019	0.023	0.084	n.d. *	0.055	n.d.
<b>C45</b>	0.48	0.22	0.70	0.012	0.038	0.12	n.d.	0.13	n.d.
<b>C60</b>	0.59	0.29	0.65	0.007	0.027	0.19	n.d.	0.093	n.d.
<b>C100</b>	0.99	0.25	0.22	0.002	0.008	0.078	n.d.	0.051	n.d.
<b>ST1</b>	0.49	2.80	0.40	0.011	0.003	8.60	0.03	0.15	97.24
<b>ST2</b>	0.15	0.05	1.34	0.068	0.287	0.12	0.03	0.08	97.67
<b>DRI</b>	1.96	0.12	0.09	0.027	0.14	0.003	n.d.	<0.001	n.d.
<b>GGG</b>	3.13	2.17	0.36	0.022	0.029	0.077	n.d.	0.056	n.d.
<b>HGG</b>	3.13	0.17	0.42	0.053	0.065	0.16	n.d.	0.23	n.d.
<b>HGM</b>	3.39	0.41	1.10	n.d.	0.105	0.34	n.d.	0.088	n.d.
<b>IWS</b>	1.29	0.41	0.75	n.d.	0.060	4.66	n.d.	0.21	n.d.
<b>S15</b>	0.45	0.28	0.78	n.d.	n.d.	2.67	n.d.	1.34	n.d.
<b>S69</b>	3.52	2.12	0.93	n.d.	n.d.	0.66	n.d.	n.d.	n.d.

(\*) n.d. = not determined and

### 3. Experimental Section

#### 3.1 Iron materials

A total of thirteen iron materials were selected and used in this study:

a) four commercially available Fe° materials for groundwater remediation termed as “DRI”, “GGG”, “HGG” and “HGM” (DRI is Eisenschwamm from ISPAT GmbH, Hamburg; GGG is Graugußeisengranulat from G. Maier Metallpulver GmbH - Rheinfelden; HGG is Hartguß-granulat from Hermens, and HGM is Hartgußstrahlmittel from Würth - all in Germany). DRI is a direct reduced iron; the other materials are cast irons from different geometrical shapes;

b) four model carbon steels termed as “C15”, “C45”, “C60” and “C100” primarily differing in their carbon content (0.15, 0.45, 0.60 and 1.00 %);

c) two selected iron materials from different classes termed as “ST1” and “ST2”. Both are mild steels, ST1 having an elevated chromium content (8.6% Cr) and ST2 an elevated sulfur content (0.287% S);

d) three scrap irons, two from a metal recycling company (Metallaufbereitung Zwickau); termed as “S15” and “S69”. S15 is a collection of mild steels from various origins and S69 a similar collection of cast irons. The third scrap iron termed as “IWS” was from the waste bin of the mechanical workshop of the Institute of Geology (Technical University Mining Academy Freiberg). IWS was a mixture of iron waste including all possible sorts of materials including stainless steel.

Apart from DRI, the commercial iron materials were used as obtained. All other samples were broken to small pieces and sieved. The experiments were then conducted with the particle sizes between 1.0 and 1.6 mm, mostly without any chemical pretreatment. Table 1 summarizes the elemental composition of the materials. The analyses were made by X-Ray fluorescence spectrometry. The data in table 1 show clearly that the materials primarily differ in their carbon (and silicon) contents. Thereafter the tested materials can be divided into three classes: GGG, HGG, HGM and S69 containing more than 3% carbon (cast irons), the seven other containing less than 2% C are mild steels whereas

DRI (1.9 % C) belongs to the third class because of the particularity of his manufacturing technology, yielding to porous materials.

On a practical point of view two classes of materials are tested: (i) materials that can be used for ground water remediation. This class included commercial Fe° materials (DRI, GGG, HGG and HGM) and the scrap irons S15 and S69 that where available in large amount; (ii) model materials that were tested to gain any hint of the influence of alloying elements on the reactivity.

Apart from HGM with a regular spherical shape, homogeneous size ( $\phi = 1.2$  mm) and smooth surface, all other materials were irregular in shape (filings and shavings) with a rough surface. DRI was of very rough surface and even porous. HGM and the two scrap irons (S15 and S69) were visibly covered with rust whereas all other samples retained their metallic glaze.

Three different particle sizes,  $d_i$  (mm) of S69 were used in this study. They were defined as:  $d_1$ ,  $d_2$ ,  $d_3$  such that:  $0.63 \leq d_1 \leq 1.0$ ;  $1.0 \leq d_2 \leq 1.6$ ;  $1.6 \leq d_3 \leq 2.5$ .

#### 3.2 Experimental procedure

Iron dissolution was initiated by the addition of 0.5 g of each material to 50 mL of a 2 mM EDTA solution (10 g/L ZVI). The experiments were conducted at laboratory temperature (about 20 °C) in narrow beaker with 70 mL total volume. The beaker were not agitated and were allowed to react been protected from direct sunlight on the laboratory desk (not in darkness). The aqueous iron concentration was recorded as a function of time.

Analysis for total dissolved iron was determined using FerroVer iron reagent (HACH DR/2000 Spectro-photometer Handbook, Loveland, CO). The used disodium salt of EDTA ( $\text{Na}_2\text{-EDTA}$ , Merck:  $M = 336.28$  g/mol) was of analytical grade.

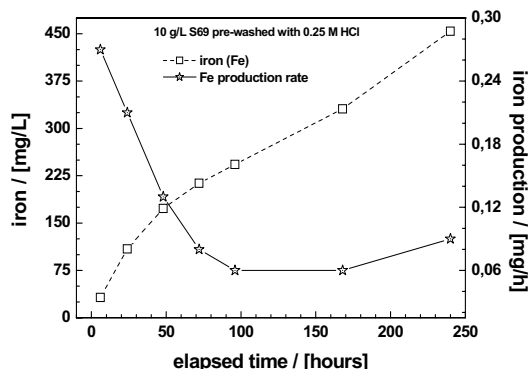
The experiments were performed in duplicates. The mean values are presented.

## 4. Results and Discussion

Preliminary works (results not shown) were conducted with EDTA concentrations varying from 0 to 100 mM and the concentration of 2 mM was selected for this study. Primary works were conducted with the scrap iron S69 because of its availability (large amount) and its rusted and rough surface. The commercial Fe° material HGM was also used in detailed investigations because of its smooth surface and its regular spherical shape.

### 4.1 Kinetics of iron dissolution

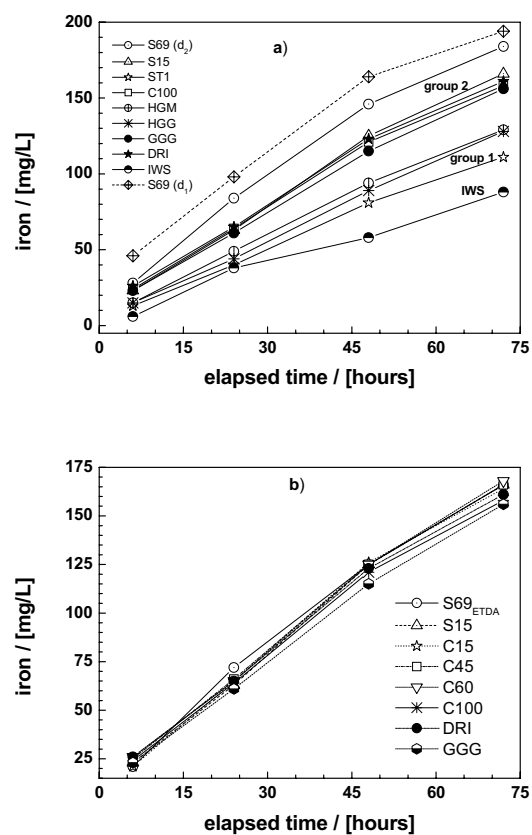
The primary work consisted in identifying the region of linearity of the iron dissolution for the selected EDTA concentration and S69. Figure 1 summarizes the variation of the iron concentration (mg/L) and the rate of iron dissolution (mg/h) as a function of time for S69 pre-washed for 14 hours in 0.25 M HCl. It can be seen that the iron concentration increases continually with the time until the end of the experiment. The plot of the rate of iron dissolution shows that iron dissolution is maximal at the beginning of the experiment and linearly decreases during the 3 first days (72 hours). During this period the color of solution changed from colorless to yellow. After three days a brown color appeared at the surface of the iron material indicating that  $\text{Fe}(\text{OH})_3$  began to precipitate. Since EDTA is not stable in light and the solutions were exposed to air oxygen, the speciation of iron in the solution at any date can not be accessed. The Fe:EDTA ratio in the system varied from 0.3 after 6 hours to 4.9 after 240 hours (10 days). After 72 hours the Fe:EDTA ratio was 2.3 in the system on Fig. 1 and 1.8 in the system where S69 was pre-washed with EDTA. This result suggests that the dissolution of iron oxides (rust) is more rapid of that of ZVI. The objective of this study is not to accurately define the systems in which the individual materials are involved, but rather to develop a technique to comparatively characterize their reactivity. Therefore, an experimental duration of 72 hours (3 days) was selected for the material characterization based on the linearity of the evolution of both the iron concentration and the rate of iron production in this time frame.



**Figure 1:** Variation of the iron concentration (mg/L) and the rate of iron dissolution (mg/h) as a function of time for S69 pre-washed for 14 hours in 0.25 M HCl. The represented lines are not fitting functions, they just joint the points to facilitate visualization.

### 4.2 Iron dissolution from tested materials

Figure 2 (a & b) and table 3 summarize the results of the iron dissolution by the tested ZVI materials. To simplify the comparison the correlation parameters were expressed in  $\mu\text{M}/\text{h}$  and  $\mu\text{M}$  respectively. From figure 2a, it can be seen that the behavior of the materials are very similar. IWS, which is a complex mixture containing stainless steel exhibits the worst iron dissolution efficiency. HGM, HGG and ST1 (group 1) exhibit a slightly better dissolution efficiency than IWS. All other materials (group 2) were very closed in their dissolution efficiency, which was the highest. A discussion on the efficiency for S69 ( $d_1$ ) and S69 ( $d_2$ ) is given in the next section, they are presented here for comparison.



**Figure 2:** Comparison of the iron production by Fe° materials for 72 hours. For clarity, only the plots for nine from the thirteen tested Fe° materials are presented in figure a). The plots for materials of group 2 are represented with a different scale in figure b). All regression parameters are listed in Tab. 3. The plots for two different particle sizes of S69 are presented. See text for the annotations (IWS, group 1, group 2). The represented lines are not fitting functions, they just joint the points to facilitate visualization.

It can be seen here that both groups from materials (group 1: HGG, HGM and ST1 and group 2: C15, C45, C60, C100, DRI, GGG, S15, S69 and ST2) include both mild steels and cast irons. From the nine materials of group 2, only five are represented for clarity in Fig. 2a; the correlation parameters are given in Tab. 3. These results confirm data from the literature that mild steel and cast iron materials corrode similarly in a wide range of aqueous environments (Piwowarsky 1951, Klas & Steinrath 1974, Uhlig 1975, Mercer & Lumbard 1995). From Tab. 3 and Fig. 2 the following efficiency order can be deduced (a-values from table 3) for non model materials:

in group 1: HGG < HGM;  
in group 2: GGG < DRI < S15 (?) < S69.

Thereafter rusted scrap irons (S15 and S69) are possibly more efficient than commercial ZVI materials. From the commercial material, porous DRI exhibits the best dissolution efficiency. Considering that DRI was additionally broken into small pieces, it is clear that the surface area is an important factor affecting the reactivity of ZVI materials. Figure 2b further shows that the nine materials from group 2 exhibit very similar iron dissolution behavior. Therefore, if the specific surface areas of the used materials are known the EDTA method can enable a more accurate material comparison and selection. Beside the surface area, the presence of rust on the surface and the microscopic topography are known to affect the reactivity of ZVI materials (Powell et al. 1995, Magnussen et el. 1998).

It should be kept in mine, that the EDTA characterizes solely the iron dissolution. This surely give an image of the reactivity, but for specific cases local site specific aspects are to be considered. For example if a satisfactorily remediation goal can be achieved with less reactive materials (group 1: HGG and HGM), then the choice between both material can be guide by the roughness of the surface. If a smooth and spherical surface is needed (to avoid) H<sub>2</sub> production, the HGM will be the best material. A similar procedure can be used to decide between DRI, GGG, S15 and S69 for group 2. Beside this aspect, specific interactions of the individual contaminants with the surface of the Fe<sup>0</sup> material have to consider (e.g. catalyze, sorption...).

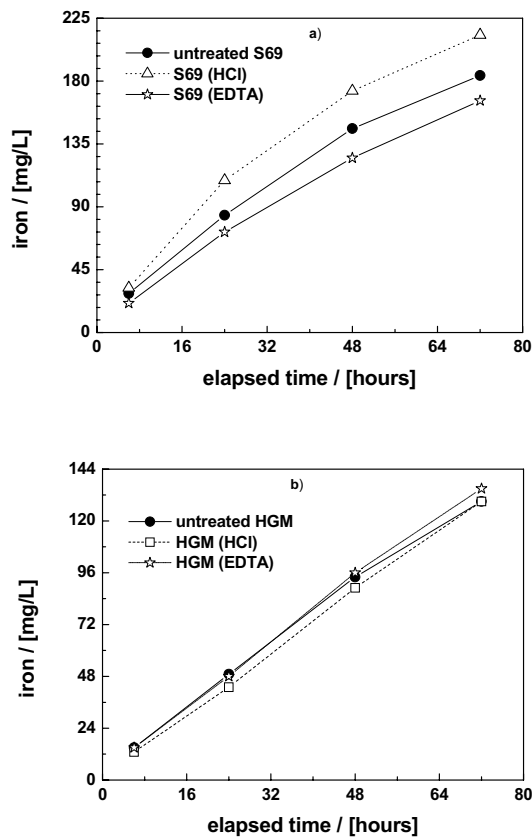
### 4.3 Effects of material pre-treatment

Two different pre-treatment methods were tested in this study: (i) a 2 mM EDTA pre-washing to eliminate corrosion products without modifying the microstructure of the material surface, and (ii) a 250 mM HCl pre-washing to completely eliminate corrosion products. HCl will possibly cause a local modification of the surface structure. Both pre-treatment methods were performed for 14 hours and the materials were further washed three times with de-ionized water before the addition of the EDTA solution. Two Fe<sup>0</sup> materials were involved in this study: a rusted scrap iron with a rough surface (S69) and a rusted commercial iron with a smooth surface, and a regular spherical shape (HGM).

**Table 3:** Correlation parameters of the straight lines  $[Fe]_t = a \cdot t + b$  of the ZVI materials in 2 mM EDTA for 72 hours a = rate of iron production, b = iron concentration at  $t_0$  and r = the correlation factor. The materials are classed from the top to the bottom in the order of increasing rate of iron production (a).

ZVI	a [mM/h]	b [mM]	r [-]
IWS	1.06	2.41	0.991
ST1	1.35	4.02	0.998
HGG	1.54	3.43	1.000
HGM	1.55	5.72	0.998
HGM <sub>HCl</sub>	1.58	1.91	1.000
HGM <sub>EDTA</sub>	1.64	4.16	0.999
GGG	1.82	11.32	0.998
C100	1.83	13.21	0.995
DRI	1.86	13.70	0.997
C15	1.92	9.03	0.995
ST2	1.94	11.71	0.995
C60	1.94	12.68	0.998
C45	1.95	12.16	0.997
S15	1.98	10.08	0.997
S69(d <sub>2</sub> ) <sub>EDTA</sub>	1.95	12.54	0.994
S69(d <sub>1</sub> )	2.03	35.94	0.985
S69 (d <sub>3</sub> )	2.06	8.48	0.996
S69 (d <sub>2</sub> )	2.12	19.20	0.990
S69(d <sub>1</sub> ) <sub>EDTA</sub>	2.36	21.47	0.978
S69 (d <sub>2</sub> ) <sub>HCl</sub>	2.41	26.75	0.981

Figure 3 (a & b) and table 3 depict the results. From Fig. 3a it can be seen that the pre-treatment of S69 induced a clear difference in the iron dissolution behavior. Whereas the pre-treatment with EDTA lowers the b-value from 19.20 to 12.54  $\mu$ M (Tab. 3). The pre-treatment with HCl enhance it rather (to 26.75  $\mu$ M) and also changes the slope (a-value from 2.1 to 2.4  $\mu$ M/h). Figure 3b and table 3 show that both pre-treatment methods did not influenced significantly the behavior of HGM. This results suggests that even the HCl pre-treatment could not sensibly promote corrodibility of this material. To properly address this question, data on the manufacture process are needed (e.g. thermal treatment). In both cases however, the differences in the b-values was clear (Tab. 3), making the EDTA-method efficient at estimating the amount of corrosion products in ZVI samples and consider them for appropriate modeling.



**Figure 3:** Effect of two different material pre-treatments (250 mM HCl and 2 mM EDTA) on the iron production by S69 (a) and HGM (b) for 72 hours. The represented lines are not fitting functions, they just joint the points to facilitate visualization.

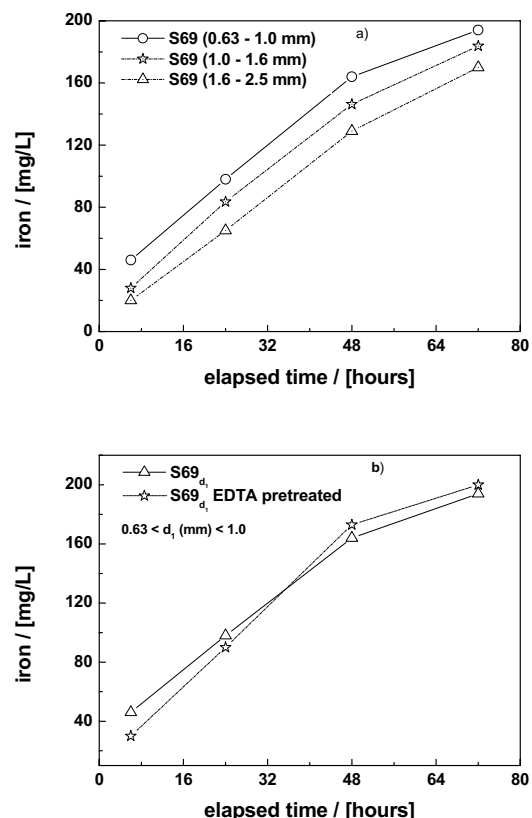
#### 4.4 Effects of the ZVI particle size

The investigation of the effects of the particle size occurred on the scrap iron S69 which was available in three different particle sizes ( $d_1$ ,  $d_2$ ,  $d_3$ ). Although the surface area was not determined, it is expected the for a given mass of material, the smaller the particle size, the higher the available surface area, and therefore the higher the dissolution efficiency.

Figure 2 has shown the plots for S69 ( $d_1$ ) and S69 ( $d_2$ ) exhibiting higher iron dissolution efficiencies than materials from group 1 and group 2. In fact the amount of released iron into the solution was higher but the iron dissolution rates were very closed (values in Tab. 3). From Tab. 3 it can be seen that the “a” values for S69 ( $d_1$ ) and S69 ( $d_2$ ) were very similar (2.03 and 2.12  $\mu\text{M/h}$ ), whereas the “b” values differed considerably (35.94 and 19.20  $\mu\text{M}$ ). Since the dissolution occur from the same untreated material with different particle sizes, it can be assumed that the fraction with the smaller particle sizes contains more corrosion products (fines), which dissolve rapidly in the EDTA solution

at the beginning of the experiment (higher b-value). After this rapid dissolution of rust (at least the reactive fraction), the dissolution of ZVI itself is uniform and characteristic for each material. This conclusion is supported by the fact that, when S69 ( $d_2$ ) was pre-washed in 2 mM EDTA, his plot coincided with that of group 2 materials in Fig. 2b, confirming his classification in this class. Apart from S15 all other material from this group where not visibly cover with rust. No experiment with pre-washed S15 was conducted. It is possible that S15 belongs to group 1 after EDTA pre-washing.

Figure 4a compares the results of the iron dissolution for three different particle sizes of S69. It can be seen that the three plots are almost parallel straight lines (same slope - Tab. 3). The difference been in the b-value ( $b = [\text{Fe}]_{\text{to}}$ ), which is a gut estimation of the amount of available reactive corrosion products. The amounts of reactive corrosion products were 35.94, 19.20 and 8.48  $\mu\text{M}$  (0.40, 0.22, 0.10 % weight) for  $d_1$ ,  $d_2$  and  $d_3$  respectively. Therefore the presence of a higher fraction of reactive iron oxides in the finest fraction of the material yielded to a rapid increased of dissolved Fe concentration which acts as limiting factor for further iron dissolution (from the  $\text{Fe}^0$ ).



**Figure 4:** Effect of two different material pre-treatments (250 mM HCl and 2 mM EDTA) on the iron production by S69 (a) and HGM (b) for 72 hours. The represented lines are not fitting functions, they just joint the points to facilitate visualization.

Figure 4b confirms this assumption since no difference in the iron dissolution could be noticed for the smallest particle size ( $d_1$ ) of S69, whether it was EDTA pre-treated or not. A similar result was reported when comparing this by the molecular hydrogen ( $H_2$ ) production in an acidic solution by the same fractions of this material (Noubactep 2003). This observation can be probably explained by the presence of noticeable amounts of well crystallized iron oxides (e.g.  $Fe_3O_4$ ) in the mass of fine corrosion products (non reactive fraction), which are more difficult to dissolve by diluted EDTA. In  $H_2$  production experiment, it was found out that the dissolution of oxide yielded to a pH increase which is a limiting factor for the  $H_2$  production. The variability and the complexity of the composition of corrosion have been documented (e.g. Ford 2002, Philipps et al. 2003). The investigation of the detailed processes responsible for the observation in Fig. 4b is over the scope of this study.

## 5. Conclusions

This study supports the fact that cast irons and mild steels have similar corrosion behaviors. Selected scrap irons could exhibit better iron dissolution efficiency than some commercial materials suggesting that they could be used instead of manufactured materials as cheap alternative. Next to the chemical composition of cast iron and middle steels, their surface state (roughness, porosity, corrosion state) are known to determine the efficiency in immobilizing contaminant. This aspect can not be addressed by the EDTA method. A larger number of parameters seem to influence the contaminant removal. Their individual effects can only be accessed by carefully manufacturing materials and testing them under relevant conditions.

Considering the specific interaction of individual contaminants with ZVI and/or with corrosion products (particularly for inorganic contaminants), the proposed method can be used as a screening test to rapidly select materials for further specific investigation. For example Noubactep et al. (2004) reported that the order of efficiency of the tested  $Fe^0$  materials for uranium total fixation was: HGG < HGM < GGG < S15 < DRI < S69, almost the same as that reported in this work. The difference is mostly due to the surface state and the affinity of uranium for generated corrosion products. In both the cases S69, GGG and DRI were to be selected at the expense of HGG and HGM.

Information generated from this study is important for the application of ZVI for remediation processes. For example to investigate the effects of coating on the reactivity of ZVI materials (Huang et al. 2003), pre-coating experiments can be performed with selected materials and the iron dissolution efficiency discussed, the reference being the system with non treated materials. In this way, this method can be further developed to gain a realistic information on many aspects of the material reactivity in the subsurface. An extension will possibly be to test other chelating agents than EDTA, particularly those with selective complexing properties.

## Acknowledgments

The authors would like to express their gratitude to Dr. R. Köber from the Institute Earth Science of the University of Kiel, who kindly purchased the commercial ZVI samples. The model steels C15, C45, C60 and C100 were purchased by Dr. Zimdars from the Institute of Material Technique of the Technical University Mining Academy Freiberg; the samples denoted as ST1 & ST2 were kindly recommended and purchased by Mr. M. Sekul from the workshop of the Institute of Geology (Technical University Mining Academy Freiberg). The scrap irons („S15“ and „S69“) was kindly purchased by the branch of the MAZ (Metallaufbereitung Zwickau, Co) in Freiberg. The work was granted by the Deutsche Forschungsgemeinschaft (DFG-GK 272).

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