

Characterising the reactivity of metallic iron in Fe⁰/As-rock/H₂O systems by long-term column experiments

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Abstract

The intrinsic reactivity of 4 metallic iron materials (Fe⁰) was investigated in batch and column experiments. The Fe⁰ reactivity was characterised by the extent of aqueous fixation of *in-situ* leached arsenic (As). Air-homogenised batch experiments were conducted for 1 month with 10.0 g/l of an As-bearing rock (ore material) and 0.0 or 5.0 g/l of Fe⁰. Column experiments were performed for 2 and 3 months. Each dynamic experiment was made up of 2 glass columns in series. The first column contained 2.5 or 5.0 g of the ore material and the second column 0.0 or 5.0 g of a Fe⁰ material. Results showed no significant reactivity difference in batch studies for all 4 materials; ZVI2 was by far the most reactive material in column experiments. This observation was attributed to the relative kinetics of production of aqueous As and Fe species under the experimental conditions and their impact on the formation of a protective film on Fe⁰. Accordingly, no protective film could be built at the surface of the least reactive materials. The results corroborated the urgent need for unified experimental procedures to characterise Fe⁰ materials.

Keywords: Column study, intrinsic reactivity, ore mineral, water treatment, zerovalent iron

Introduction

Elemental metals are efficient reactive agents for the remediation of several classes of environmental contaminants including arsenic, azo dyes, bacteria, halogenated organic compounds, heavy metals, nitrates, nitroaromatics, radionuclides, and viruses (O'Hannesin and Gillham, 1998; Bojic et al., 2004; Bartzas et al. 2006; Bojic et al., 2007; Henderson and Demond, 2007; Komnitsas et al. 2007; Bojic et al., 2009; Antia, 2010; Bartzas and Komnitsas, 2010; Bundschuh et al., 2010; Luna-Velasco et al., 2010; Noubactep, 2010a; Phillips et al., 2010; Sarathy et al., 2010; Comba et al., 2011; Giles et al., 2011; ITRC, 2011; Lin et al., 2011; Noubactep, 2011a; Salter-Blanc et al., 2011). Metallic iron (Fe⁰) is currently the most used material for field applications (Gillham, 2010; Comba et al., 2011; Gheju, 2011; Henderson and Demond, 2011; ITRC, 2011; Salter-Blanc et al., 2011).

Despite the wide variety of environmental contaminants and their possible specific interactions with Fe⁰, tested materials were characterised mainly by their surface area, size and interface chemistry (e.g. surface state). However, it has been traceably demonstrated that none of these structural and physical characteristics is really determinant for the chemical reactivity of Fe⁰ (Reardon, 1995; Landis et al., 2001; Noubactep et al., 2005; Reardon, 2005; Noubactep et al., 2009). For instance, Landis et al. (2001) reported that Fe⁰ materials of comparable particle size (comparable surface area) exhibited reactivity differences greater than 3-fold for cDCE and VC degradation rates in column studies. This example substantiates that a broad understanding of the chemical reactivity is urgently needed.

Several sources of Fe⁰ materials have been reported in literature to be efficient for aqueous contaminant removal (Landis et al., 2001; Miehr et al., 2004; Leupin and Hug, 2005; Noubactep et al., 2005; Gheju and Iovi, 2006; Satapanajaru et al., 2006; Yang et al., 2006; Ngai et al., 2007; Gheju et al., 2008; Gheju and Balcu, 2010; Gheju and Balcu, 2011, Wanner et al. 2011). These include commercial Fe⁰ for contaminant removal (e.g. Connelly iron, Peerless iron, iron from G. Maier GmbH), commercial iron for other purposes (e.g. construction steel, iron nails, steel wool), scrap iron, production by-products, and Fe⁰ prepared *in situ* by reduction of iron salts. Although many tested materials have been reported to be highly reactive and recommendable for field application, efficacy of Fe⁰ in terms of high removal capacity for a specific contaminant in short-term experiments is not a guarantee for high removal capacity in field applications. Moreover, researchers working with nano-scale Fe⁰ usually compare their results to that of conventional micro-scale Fe⁰ (Noubactep et al., 2012 and references cited therein). The question is what is the reference material to which innovative materials should be compared?

The present study is a continuation of a series of works aiming at introducing reliable tools for the evaluation of the intrinsic reactivity of various Fe⁰ materials. A method based on the characterisation of Fe dissolution in a 2 mM EDTA solution was first proposed (Noubactep et al., 2004; 2005; 2009). The method was proven less efficient for powdered materials and for materials with high proportion of fines (Noubactep, 2010b). On the other hand, Fe⁰ dissolution is not necessarily coupled to contaminant removal. These limitations have led to the development of a second experimental tool in which Fe⁰ is characterised by the extent of the discoloration of methylene blue (MB) in the presence of manganese dioxide (MnO₂) (MB-test) (Noubactep, 2009). The MB-test was shown to be more efficient and affordable than the EDTA-test but was limited by the lack of reference MnO₂ materials. Both tests could enable an advanced material screening. However, of the 18 tested materials, 7 were still

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Received 3 June 2011; accepted in revised form 28 June 2012.

exhibiting very similar reactivity. Therefore, new approaches are needed.

A further possibility to characterise the reactivity of Fe⁰ materials is to stress them in systems where building of a protective film at their surface is likely to occur. Such a system was identified recently while characterising the solubilisation of toxic species from natural rocks (Noubactep et al., 2008a; 2008b). It was shown that elevated amounts of As could be leached from an ore material for a long time (up to 99 days). Accordingly, introducing the same amount of various Fe⁰ materials in a system capable of producing As concentrations as high as 1 000 mg/l could be a powerful tool to investigate the impact of As on the formation of the oxide film (mixed oxides) in the process of contaminant removal by Fe⁰. As a rule, the more reactive a material, the more rapid the passivation process (protective film formation). In other words, the system with the most reactive material will exhibit the lowest contaminant removal efficiency.

The objective of this study is to present a new contribution to the effort for the development of reliable protocols for the comparison of the intrinsic reactivity of different Fe⁰ materials. For this purpose, 4 selected materials from former works were tested. One of the materials was essentially less reactive than the others. The three other materials were very closely matched in their reactivity by both tests described above (Noubactep, 2010b). The results confirmed the suitability of the used method and opened new routes for coupling the investigation of contaminant release and contaminant removal under relevant conditions.

Materials and methods

Solid materials

As-bearing rock

The As ore material used originates from the Otto-Stollen in Breitenbrunn/Erzgebirge (Saxony, Germany). The material was selected on the basis of its high arsenic content (80%). A qualitative SEM analysis showed the presence of As, Ca, F, Fe, O, S and Si (Noubactep et al., 2008). The ore material is primarily a hydrothermal vein material and arsenic occurred as native arsenic (As⁰) and Loellingite (FeS₂ - As⁻¹) (Jones and Nesbitt, 2002) in paragenesis with hydrothermal vein carbonates (for example Fe-bearing calcite or dolomite). The mineral was ground and sieved. The particle size fraction 0.063 ≤ d (mm) ≤ 0.10 was used without any pre-treatment.

Fe⁰ materials

One scrap iron (ZVI1), and three commercially-available Fe⁰ materials were tested. The main characteristics of these materials are summarised elsewhere (Noubactep, 2010b). ZVI2 is a spherical material (d = 1.2 mm) from Würth (Germany) termed ‘Hartgußgranulat’. ZVI3 are iron chips from G. Maier GmbH

Rheinfelden (Germany) termed ‘Graugußgranulat’. ZVI4 is a direct reduced iron from ISPAT GmbH (Germany), termed ‘Schwammeisen’. Before use ZVI4 was crushed and sieved; the size fraction 1.0–2.0 mm was used. The specific surface area of the materials varies between 0.043 and 0.63 m²/g. These data were compiled from the literature (Table 1). The materials were compared solely on the basis of the extent of As removal by the same initial mass of Fe⁰ (e.g. 5.0 g in columns) under similar experimental conditions. The materials differ regarding their characteristics, such as iron content, nature and proportion of alloying elements, and shape.

The 4 materials used were selected from 9 materials which were recently characterised by leaching with 2 mM EDTA in column study (Noubactep, 2010b). In turn, the 9 materials tested were selected from 18 materials after screening in batch experiments using the EDTA-test (Noubactep et al., 2005; Noubactep et al., 2009). Both tests could not really differentiate the reactivity of ZVI1, ZVI3 and ZVI4. The reactivity of these three materials toward As removal from a natural rock was investigated in this study. For comparison the least reactive commercial Fe⁰ (ZVI2) was incorporated in this study.

Sand

The sand used was a commercial material for aviculture (“Papagaiensand” from RUT – Lehrte/Germany). Papagaiensand was used as received without any further pre-treatment or characterisation. This sand was the operational reference non-adsorbing material.

Leaching solution

The leaching solution was tap water of the city of Göttingen (Lower Saxonia, Germany). Tap water is considered to be a better proxy for natural groundwater than synthetic solutions (Noubactep, 2003; Noubactep et al., 2008). The rationale behind this assumption is that, in many cases, natural water is only treated for iron and manganese removal. The average composition (in mg/l) of the tap water used was: Cl⁻: 7.7; NO₃⁻: 10.0; SO₄²⁻: 37.5; HCO₃⁻: 88.5; Na⁺: 7.0; K⁺: 1.2; Mg²⁺: 7.5; Ca²⁺: 36.1; and an initial pH of 8.3.

As leaching and immobilisation

Air-homogenised batch experiments

These experiments were conducted in special reaction vessels allowing the system to be homogenised by a humid current of air supplied by a small aquarist pump. The goal was to homogenise the experimental systems at atmospheric pressure ($P_{\text{CO}_2} = 0.035\%$) without breaking down the materials. 10.0 g/l of the ore material and 0.0 or 5.0 g/l of Fe⁰ were allowed to react in sealed vessels containing 100 ml of tap water at laboratory temperature (22 ± 3°C) for up to 30 days. At given dates, 1.5 ml of the solution was retrieved and diluted for As analysis and the same volume of tap water was added to the system.

ZVI	Element (%)							SSA (m ² /g)
	C	Si	Mn	Cr	Mo	Ni	Fe	
ZVI4	1.96	0.12	0.09	0.003	n.d.	<0.001	86.3	0.63
ZVI2	3.39	0.41	1.10	0.34	n.d.	0.088	91.5	0.043
ZVI1	3.52	2.12	0.93	0.66	n.d.	n.d.	99.8	0.29
ZVI3	3.13	2.17	0.36	0.077	n.d.	0.056	96.7	0.50

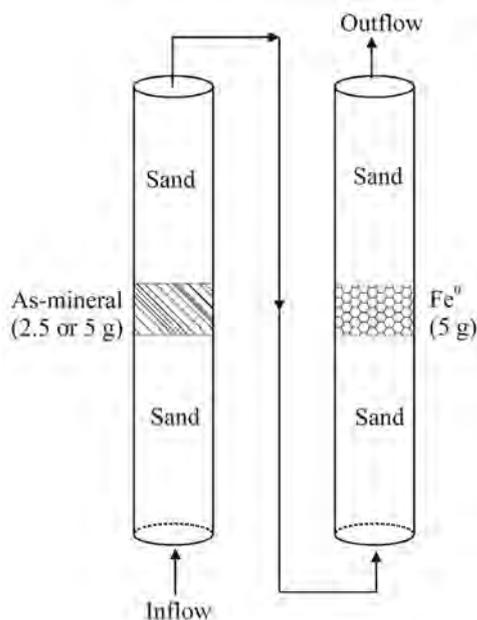


Figure 1
Schematic diagram of the experimental design for the 2-column studies. Materials used were As mineral (2.5 or 5.0 g) and Fe⁰ (5.0 g).

Column experiments

The tap water was pumped upwards from PE bottles using a peristaltic pump (Ismatec, ICP 24). Tygon tubes were used to connect inlet reservoir, pump, column and outlet. Ten glass columns (40 cm long, 2.6 cm inner diameter) were used in two series of experiments. The columns were mostly packed with sand. The effective length, bulk density and porosity of the packed columns were not characterised as this was not necessary for the discussion of the results. The extent of As dissolution by water and the extent of its removal by selected Fe⁰ materials were the sole targets. The experiments were performed at room temperature (22 ± 3°C). A stable flow rate was maintained throughout the experiment.

Five parallel experiments were performed in each series. The same mass of the rock (2.5 or 5.0 g) was placed in a first column and 5.0 g of each tested Fe⁰ was placed in the second column (Fig. 1). In the reference system, the second column contained only sand (no Fe⁰). The experiments were stopped after 65 or 97 days when each column was leached by 19 or 25.0 l of tap water (Table 2). The water flow rate was constant at 12.0 ml/h.

		Batch	Column 1	Column 2
Duration	(d)	30.0	65.0	97.0
As-mineral	(g)	1.0	5.0	2.5
ZVI	(g)	0.5	5.0	5.0
V _T	(l)	0.1	19.0	25.0
Flow rate	(ml/h)	Air-bubbled	11.9	11.9

Analytical methods

Analysis for As was performed by inductively coupled plasma mass spectrometry (ICP-MS) at the Department of Geochemistry (Centre of Geosciences, University of Göttingen). All chemicals used for the experiments and analyses were of analytical grade. The pH value was measured by combining glass electrodes (WTW Co., Germany). The electrodes were calibrated with 5 standards following a multi-point calibration protocol and in agreement with the new IUPAC recommendation (Meinrath and Spitzer, 2000; Buck et al., 2002).

Expression of experimental results

The mass (*m*) of leached As (mg) at any time (*t*) is calculated from the concentration of the effluent using Eq. (1):

$$m = P \cdot V \quad (1)$$

where

P is the As concentration (in mg/l) and
V the volume (l).

At the end of the experiment the total amount of leached As can be calculated by addition and the extent of As leaching by tap water deduced. Knowing the As percentage in the natural rock (80%), the maximal leachable mass (*m*₀) of As can be calculated. The percentage (*P*) As leaching at each time is given by Eq. (2):

$$P = 100 \cdot m / m_0 \quad (2)$$

At each time the amount of As leached in the reference system (*P*_{ref}) can be set to 100 and the relative leaching percent (*P*_{rel}) for all other systems deduced by Eq. (3):

$$P^* = P_{rel} = 100 \cdot P / P_{ref} \quad (3)$$

Finally, the relative percentage of As removal (*P*_{fix}) by each material is given by Eq. (4):

$$P_{fix} = 100 - P_{rel} \quad (4)$$

Results and discussion

The particularity of the As-rock/Fe⁰ systems investigated here is that aqueous As and the solid Fe hydroxides and oxides for their removal are generated *in situ*. It has been traceably demonstrated, that As^{III} and As^V are removed in Fe⁰/H₂O systems by adsorption and co-precipitation (Lackovic et al., 2000; Farrell et al., 2001; Noubactep, 2010a; Noubactep, 2011b; Noubactep, 2011c; Noubactep, 2012). As released from the ore material used was recently characterised (Noubactep et al., 2008a) and the process of As dissolution will not be discussed here. The basis for the characterisation of Fe⁰ materials is that the smallest As concentration (relative to the reference system) is encountered in the system with the most reactive material under testing conditions.

Batch experiments

Figure 2 illustrates As dissolution in the absence (reference) or presence of tested Fe⁰ materials (ZVII through ZVI4), as a function of time. Both leaching kinetics and the extent of As

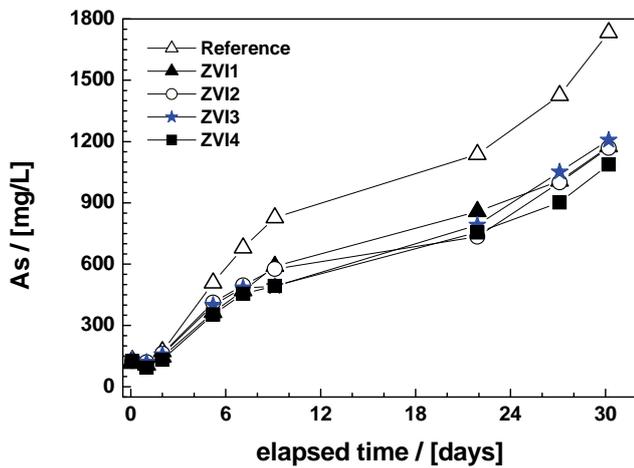


Figure 2

Arsenic release (mg/l) from the base material as a function of time in air-homogenised batch experiments. The lines are not fitted functions; they simply connect points to facilitate visualisation.

	Batch		Column 1		Column 2	
	m (mg)	P_{fix} (%)	m (mg)	P_{fix} (%)	m (mg)	P_{fix} (%)
Reference	173	0.0	338	0.0	3 745	0.0
ZVI1	118	32.2	307	9.1	2 985	20.3
ZVI2	117	32.6	243	28.0	2 782	25.7
ZVI3	121	30.4	322	4.6	3 301	11.9
ZVI4	109	37.3	322	4.6	3 306	11.7

release substantially decreased with the addition of Fe⁰. From Fig. 2 no difference in reactivity can be visually detected. It appears that the reactivity of all 4 materials is very similar. Examination of the P_{fix} values (Table 3) shows that the relative fixation efficiency varies from 30.4 to 37.3 %. A tentative order of increasing reactivity based on these values is: ZVI3 < ZVI1 < ZVI2 < ZVI4. Note that the order of reactivity after the EDTA-test (Noubactep et al., 2005; 2009) and the MB-test (Noubactep, 2009) were univocally: ZVI2 < ZVI1 = ZVI3 = ZVI4. Accordingly, air-homogenised batch experiments are not appropriate for the differentiation of the reactivity of ZVI1, ZVI3 and ZVI4. It is well known that batch systems cannot accurately reflect processes occurring in nature (Wang et al., 2009). The first reason for this, in regard to the experimental conditions of this work, is the possibility of super-saturation of the As solution given the excessive contact time (30 days) and the relatively strong homogenisation with air-bubbles. To account for this, further characterisations were performed under dynamic conditions.

Column experiments for 65 days

Figure 3a shows the effect of tested ZVIs on As leaching from the natural ore as a function of time (≤ 65 days). 5.0 g of the

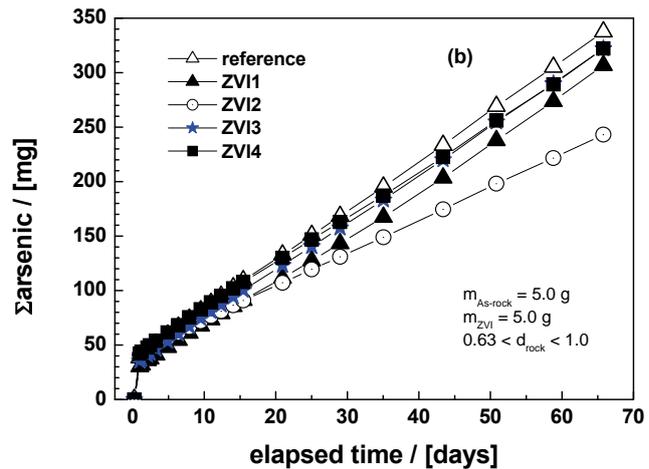
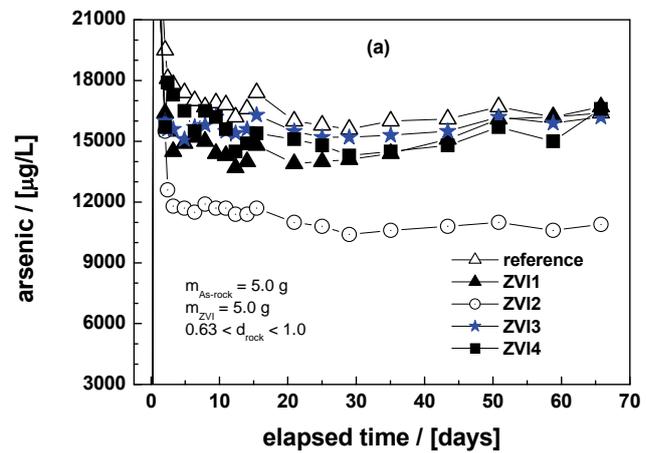


Figure 3

Extent of arsenic release from the 2-column systems for 65 days by tested Fe⁰ materials: (a) variation of the extent of As release with time, and (b) cumulative As release (mg). The lines are not fitted functions; they simply connect points to facilitate visualisation.

ore material was placed in the first column and 5.0 g of ZVI1 in the second column (Fig. 1). From Fig. 3a a visual differentiation of ZVI2 is evident. It is also evident that the reference system exhibited the highest As concentration. The cumulative sum of released As (Fig. 3b) confirmed this trend. The m - and P_{fix} -values (Table 3) confirmed these observations. The deduced order of increasing reactivity is: ZVI3 = ZVI4 < ZVI1 < ZVI2. This classification, showing that ZVI2 was the most reactive material, is acceptable, but the experimental conditions should be further modified to obtain a clear trend. The following modifications were made:

- the mass of ore material was halved;
- the first 2 l of leaching solution in Fe⁰/As-rock systems was discarded; and
- the duration of the experiment was lengthened to 97 days.

All other parameters (flow rate, temperature) were kept constant. The rationale behind discarding the first 2 l of leaching solution was the elevated As concentration which occurred in this initial phase (Fig. 3a).

The next important feature to note from Fig. 3a is that 5.0 g of the used ore material is capable of producing about 17 mg/l (reference system) As for more than 2 months. High As concentration was intentionally tested here. By varying the mass

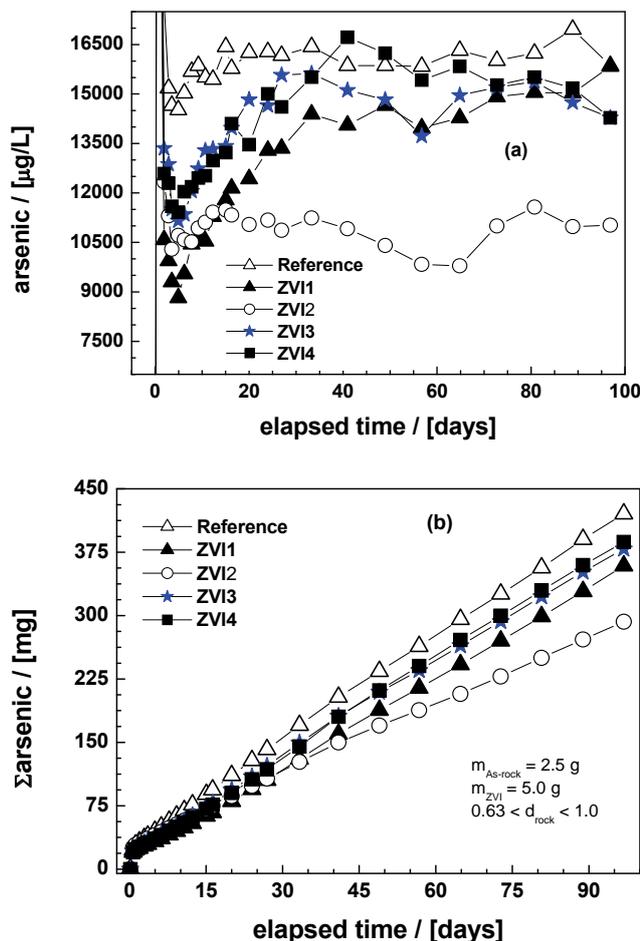


Figure 4

Extent of arsenic release from the 2-column systems for 97 days by tested Fe^0 materials: (a) variation of the extent of As release with time, and (b) cumulative As release (mg). The lines are not fitted functions; they simply connect points to facilitate visualisation.

of the ore material and the particle size, As concentrations relevant for each specific size could be achieved.

Column experiments for 97 days

Figure 4a shows the effect of tested ZVIs on As leaching from the natural ore as a function of time (≤ 97 days). A visual reactivity difference can be better performed than in Fig. 3a. The visual increasing order of reactivity is: $\text{ZVI4} < \text{ZVI3} < \text{ZVI1} < \text{ZVI2}$. The m - and P_{fix} -values shown in Table 3 confirmed this trend, with the additional information that ZVI3 and ZVI4 are very closely matched in their reactivity, as the per cent As removal (P_{fix} -values) for each was 11.9 and 11.7, respectively. Figure 4b clearly confirmed the results shown in Table 3.

From Fig. 4a is clear that 2.5 g of the As-rock is able to produce about 16 mg/l As for more than 3 months. These results clearly show that long-term experiments regarding As removal can be coupled with As leaching from natural ores. By reducing the ore mass, changing the particle size and using different ores it is possible to perform long-term leaching experiments in the laboratory. Such experiments could help to bridge the huge gap between the laboratory and the field (Wang et al., 2009). On the other hand, parameters from

such systems could help to develop more reliable models to predict contaminant leaching in the environment.

Discussion

The use of Fe^0 materials for environmental remediation is severely handicapped by the lack of methods for characterisation of the chemical reactivity. The current procedure of testing the reactivity of Fe^0 for individual contaminants (Landis et al., 2001; Miehr et al., 2004; Leupin and Hug, 2005; Gheju and Iovi, 2006; Wanner et al. 2011) is not very useful as no comparison between two independent works is possible, even for the same contaminant. Ideally, there should be a universally-acceptable/accepted method to evaluate various Fe^0 for their chemical reactivity. Accordingly, it is contemplated to propose protocols, which could be used to compare the efficiency of different Fe^0 .

From available works, only the characterisation of Fe^0 by the extent of H_2 production (Reardon, 1995; 2005) could be regarded as a universally applicable method to characterise Fe^0 intrinsic reactivity. However, this protocol is not necessarily affordable and uses relatively high Fe^0 masses (15.0 to 400 g). Accordingly, more simple and affordable tests should be developed. The EDTA-test (Noubactep et al., 2005; 2009) and the MB-test (Noubactep, 2009) are simple and affordable but they could not address the passivation of tested material.

By using elevated As concentrations, the present work has corroborated warnings to perform contaminant removal experiments with over-saturated solutions (e.g. Kalin et al., 2005). However, in addition to the instability of used solutions introducing biases in the extent of contaminant removal by the tested process, this study has delineated the impact of elevated concentrations on the passivation process. In fact, in nature contaminants are rarely available at high concentration (Henderson and Demond, 2011; Kümmerer, 2011) and contaminated water enters the zone containing Fe^0 when an oxide scale is already formed at its surface. In other words, while using elevated contaminant concentrations, an artificial system is created that could not be reproduced in nature. On the other hand, elevated contaminant concentrations necessarily impact the process of film formation on Fe^0 (Noubactep, 2010c).

Concluding remarks

In an attempt to access their intrinsic chemical reactivity, the performance of 3 commercial Fe^0 (ZVI2, ZVI3 and ZVI4) and 1 scrap iron (ZVI1) for the removal of As was evaluated in long-term column studies. As was leached from a natural rock using the tap water of the city of Göttingen as leaching solution. The results confirmed findings from previous works that ZVI2 is the least reactive material (Noubactep et al., 2005; 2009; Noubactep, 2010a, Noubactep 2011d). It could further be shown that ZVI1 is less reactive than ZVI3 and ZVI4.

The test methodology consisting of leaching As with tap water can be further improved or adapted to investigate several aspects of contaminant release and contaminant removal. For example, by reducing the mass of the ore material As concentrations relevant to field situations could be obtained and used to characterise the performance of Fe^0 materials for As removal. On the other hand, using several leaching solutions could enable the characterisation of the impact of relevant ions on the process of As leaching (and/or removal). Such experiments could be designed on the basis

of site-specific situations. It is hoped that this new experimental tool will accelerate efforts to characterise the intrinsic reactivity of Fe⁰ materials.

Acknowledgments

The arsenic-bearing ore used was purchased by the Department of Geology of the Technical University Bergakademie Freiberg. Dr. Klaus Simon (Centre of Geosciences, University of Göttingen) is acknowledged for the As analysis. Dr. Ralf Köber (Institute Earth Science of the University of Kiel) kindly purchased the commercial ZVI samples. The scrap iron (Sorte 69) was kindly purchased by the branch of the MAZ (Metallaufbereitung Zwickau, Co) in Freiberg. Mohammad Azizur Rahman (Angewandte Geologie, Universität Göttingen) is acknowledged for technical support. The work was supported by the Deutsche Forschungsgemeinschaft (DFG-No 626/2-2).

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