



Characterizing the reactivity of metallic iron in Fe⁰/EDTA/H₂O systems with column experiments

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ARTICLE INFO

Article history:

Received 28 April 2010

Received in revised form 9 June 2010

Accepted 10 June 2010

Keywords:

Column study

EDTA

Electrochemical reactivity

Water remediation

Zerivalent iron

ABSTRACT

Characterizing the intrinsic reactivity of iron materials for environmental remediation has received relative little interest. Available results are mostly based on the removal extent of selected contaminants in batch systems. Under static conditions however, contaminant removal depends on the properties of the oxide-film. The present study was performed to investigate the chemical reactivity of nine Fe⁰ materials under conditions that minimize the formation of an oxide-film on the metal surface. Ethylenediaminetetraacetate (EDTA) was used to sustain Fe⁰ dissolution during column testing for 2 months. The results confirm Fe⁰ dissolution rate in 2 mM EDTA as a good tool for comparative reactivity characterization. Moreover, long-term column studies with 2 mM EDTA enable: (i) the evidence of increased powdered Fe⁰ reactivity relative to granular materials and (ii) a clear differentiation among granular materials which exhibited very closed extents of iron dissolution under static conditions. Future works comparing Fe⁰ intrinsic reactivity should ideally characterize material behaviour in an oxide-free system and compare the results to those obtained under relevant experimental conditions.

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1. Introduction

Iron-based permeable reactive barriers (iron walls) have been successfully used as an efficient in situ remediation technology for groundwaters contaminated with various organic and inorganic compounds over the past 15 years [1–5]. The real mechanism of contaminant removal is yet to be elucidated. Despite a broad consensus on reductive transformations [1], quantitative contaminant removal by other mechanisms has been reported. Currently, it is assumed that Fe⁰/H₂O systems may remove chlorinated organics by reductive degradation, whereas metals, metalloids and radionuclides may be removed via reductive precipitation, surface adsorption or complexation, or co-precipitation with the Fe oxyhydroxides that are generated in the system [2–4]. The validity of this concept is progressively questioned [6–12]. In fact, some of the enumerated processes must be fundamental and valid for all possible pollutants while others will be valid only in particular situations (e.g. the contaminant is reducible). In addition to the diversity of successfully removed contaminants in Fe⁰/H₂O systems, there is diversity among Fe⁰ sources (intrinsic properties) and thus diversity in the chemical reactivity of used materials.

Over the past 20 years Fe⁰ materials used in laboratory and field Fe⁰/H₂O systems were available from a variety of commer-

cial sources including [13–15]: (i) chemical reagents (e.g. Merck, Across, Aldrich), (ii) untreated scrap iron and by-products [15,16], and (iii) Fe⁰ materials manufactured for environmental remediation (e.g. Connelly-GPM Inc., G. Maier GmbH, ISPAT GmbH, Peerless Metal Powders & Abrasive). The results of experiments using such different materials have been compared to each other with little care on the intrinsic material reactivity (see next section). To date there is no standard parameter to evaluate the intrinsic reactivity of Fe⁰ materials [17]. However, it is well known that, the metal type and method of manufacture are as important as the environment (solution corrosiveness) for corrosion processes [18]. Clearly, the presence and amount of alloying and other foreign elements, the size of the material, and whether the metal is cast, forged, wrought or welded are critical to material intrinsic reactivity (corrodibility). A further problem with the majority of commercially available Fe⁰ is that the materials are produced from scrap iron and steel obtained from a number of primary industries using iron in the production of automotive and related industrial parts [13]. Therefore, the “feedstock” for commercially available Fe⁰ is a mixture including scrap iron and steel. The mixture is heated at 700–1200 °C in rotary kilns to burn off the non-metallic materials, especially the cutting oils [13]. Accordingly, the real manufacturing history of commercially available Fe⁰ is not traceable. This is the major reason why materials should be characterized “as received”.

Factors affecting Fe⁰ reactivity in laboratory experiments can be divided into three subgroups: (i) material-dependent factors (intrinsic reactivity – mostly not directly accessible to researchers),

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(ii) environment-dependent factors (investigable at individual relevant sites), and (iii) operational experimental parameters (should be designated to mimic environment-dependent factors). Environment-dependent factors and operational experimental parameters are not addressed in the present work. As concerning material-dependent factors, they include: Fe⁰ manufacturing history, Fe⁰ elemental composition, Fe⁰ particle size (nm, μm, mm), Fe⁰ surface area and surface property (also of generated oxides). A decade of investigations on Fe⁰ have not clarified the relative importance of the individual factors of this subgroup [15,19,20]. However, an unjustified importance was attributed to one of these parameters: the surface area [19,21] and kinetic rate constant (k_{obs}) are usually normalized to the surface area [22,23]. To characterize the Fe⁰ intrinsic reactivity, most of the tested materials were used without any pretreatment (“as received”). Only one material was crushed and sieved to yield particle size relevant for field applications (≤ 2 mm). Their chemical reactivity is evaluated as the extent of iron dissolution in the presence of ethylenediaminetetraacetate (EDTA available as Na₂-EDTA).

The ability of EDTA to sustain iron oxidative dissolution is well documented in the corrosion science [24–26] and has been used to avoid the formation of oxide-film on Fe⁰ in experiments investigating contaminant removal in Fe⁰/H₂O systems [27–29]. A comprehensive discussion on the chemistry of the Fe⁰/EDTA/H₂O system is given by Pierce et al. [30]. Previous works characterizing the reactivity of Fe⁰ in the presence of EDTA (2 mM) showed that the kinetic rate constant of iron dissolution (termed k_{EDTA}) is a useful parameter to differentiate the reactivity of Fe⁰ materials in batch systems [15]. To further characterize the reactivity of Fe⁰ in batch experiments, a parameter τ_{EDTA} was introduced [31,32]. Per definition, τ_{EDTA} is the time necessary to reach aqueous Fe saturation under given experimental condition assuming 1:1 Fe/EDTA complexation ([Fe] = 2 mM or 112 mg L⁻¹).

The objective of the present work was to investigate the feasibility of using EDTA to characterize the reactivity of Fe⁰ materials in column studies. For this purpose a series of nine pre-selected Fe⁰ materials are used. Their chemical reactivity in a 2-mM EDTA solution is comparatively examined. The extent of iron dissolution in individual columns is used to assess Fe⁰ reactivity. For the sake of clarity the definition of chemical reactivity will be recalled.

2. Electrochemical reactivity of Fe⁰

In discussing the suitability of Fe⁰ for environmental remediation one has to properly distinguish between the corrodibility of Fe⁰ and the corrosiveness of the aqueous environment. Fe⁰ corrodibility is the material's susceptibility to corrosion or the material's intrinsic chemical reactivity. Because iron corrosion is primarily an electrochemical process, Fe⁰ intrinsic reactivity can be regarded as Fe⁰ electrochemical reactivity. The corrosiveness of the environment refers to the aggressiveness of the aqueous solution toward Fe⁰ oxidative dissolution. Consequently, Fe⁰ corrodibility and solution corrosiveness are not objective parameters but subjective tendencies. Accordingly, the Fe⁰ electrochemical reactivity is its tendency to undergo an oxidative dissolution. Similarly, the corrosiveness of a contaminant for a given Fe⁰ material is its ability to induce oxidative dissolution of the material. Efforts to characterize electrochemical reactivity of Fe⁰ in neutral and close-to-neutral solutions are complicated by two major parameters: (i) the formation of oxide layers on Fe⁰, and (ii) the interactions of dissolved species within the oxide layers. Therefore, efforts have been made to characterize iron-corrosion-related processes in the absence of oxide layers [15,26,30,31]. One of these efforts is used in this study. It consists in using EDTA as chelating agent to avoid the formation

Table 1

Origin, name and main characteristics of tested Fe⁰ materials.

Origin	Original denotation	Code	Form	\varnothing (μm) ^a
MAZ, mbH	Sorte 69 ^b	ZVI6	Filings	80–4000
G. Maier GmbH	FG 0300/2000	ZVI1	Filings	200–2000
G. Maier GmbH	FG 1000/3000	ZVI4	Filings	1000–3000
Würth	Hartgußstrahlmittel	ZVI5	Spherical	1200
Hermens	Hartgußgranulat	ZVI2	Granular	1500
G. Maier GmbH	Graugußgranulat	ZVI7	Chips	350–1200
ISPAT GmbH	Schwammeisen	ZVI3	Filings	9000
Connelly-GPM	ETC-CC-1004	ZVI9	Filings	500–1000
ACROS	Fe, powder, 99%	ZVI8	Powder	45

^a Average values from material supplier.

^b Scrap iron material.

of oxide layers on Fe⁰ and thus, to sustain Fe⁰ oxidative dissolution by molecular O₂ (and H₂O).

The presentation above shows clearly that each Fe⁰ material is characterized by its electrochemical reactivity and each contaminant by its corrosiveness for a given Fe⁰. More precisely, a given concentration of a contaminant (in a given solution – ionic strength, pH value) exhibits a certain corrosiveness for a given Fe⁰. The difficulty arises when one has to compare data obtained by various investigators under different experimental conditions even when the experiments would have used the same mass loading of a given Fe⁰ material [32]. To take these weaknesses into account, the present study comparatively investigates the kinetics and the extent of Fe⁰ oxidative dissolution by molecular O₂ (and H₂O) in the presence of EDTA for nine materials in column experiments.

3. Materials and methods

3.1. Solutions

Based on previous works, a working EDTA solution of 0.002 M was used [15,31,32]. Working EDTA solutions (0.02 M or 2 mM) was obtained by a one step dilution (1:20) of a stock solution prepared from an analytical grade chemical (ethylenediaminetetraacetic acid di-sodium salt – ACROS Organics). A standard iron solution (1000 mg L⁻¹) from Baker JT[®] was used to calibrate the Spectrophotometer. The reducing reagent for Fe^{III}-EDTA was ascorbic acid. The ascorbic buffer was used to keep the pH <4.0. 1,10 orthophenanthroline (ACROS Organics) was used as reagent for Fe^{II} complexation. Used L(+)-ascorbic acid and L-ascorbic acid sodium salt were of analytical grade. All solutions were prepared using deionised water.

3.2. Fe⁰ materials

One laboratory grade iron powder (ACROS Organics - ZVI9), one scrap iron (ZVI7), and seven commercially available iron materials have been tested. Table 1 summarizes the main characteristics of these materials together with their iron content. Before used ZVI3 was crushed and sieved; the size fraction 1.0–2.0 mm was used without any further pretreatment. The specific surface area of the materials varies between 0.043 and 1.8 m² g⁻¹. These data were compiled from the literature (Table 1). The objective of this study is to compare the materials in the form in which they could be used in field applications. Accordingly, the materials were compared mostly on the basis of the extent of iron dissolution from the same initial mass of Fe⁰ (1.0 g) by the same volume of 2 mM EDTA. Apart from ZVI3, all other materials were used as obtained. Crushing and sieving ZVI3 aimed at working with materials of particle size relevant for field applications. The materials differ regarding their characteristics such as iron content, nature and proportion of

Table 2

Elemental composition and specific surface area (SSA) of iron materials used in this study. n.a. = not available and n.d. = not determined.

ZVI	Elemental (%)							SSA (m ² g ⁻¹)
	C	Si	Mn	Cr	Mo	Ni	Fe	
ZVI1 ^a	3.2	1.95	n.a.	0.023	n.a.	0.02	92.00	0.048 ^b
ZVI2	3.13	0.17	0.42	0.16	n.d.	0.23	96.7	0.50 ^c
ZVI3	1.96	0.12	0.09	0.003	n.d.	<0.001	86.3	0.63 ^d
ZVI4 ^a	3.2	1.95	n.a.	0.023	n.a.	0.02	92.00	0.048 ^b
ZVI5	3.39	0.41	1.10	0.34	n.d.	0.088	91.5	0.043 ^c
ZVI6	3.52	2.12	0.93	0.66	n.d.	n.d.	99.8	0.29 ^e
ZVI7 ^a	3.13	2.17	0.36	0.077	n.d.	0.056	96.7	0.50 ^f
ZVI8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	99.0	n.a.
ZVI9 ^a	2.85	1.85	0.60	0.10	0.15	0.13	89.82	1.8 ^g

^a Data of elemental composition from supplier.^b Ref. [33].^c Ref. [34].^d Data from supplier.^e Ref. [35].^f Ref. [36].^g Ref. [37].

alloying elements, and shape. No information about the manufacture process (e.g. raw material, heat treatment) was available.

A survey of the elemental composition (Table 1) shows that the tested materials primarily differ in their carbon (and silicon) contents. Thereafter the tested materials can be divided into three classes: (i) ZVI1, ZVI2, ZVI4, ZVI5, ZVI6 and ZVI7 containing more than 3% carbon (cast irons), (ii) ZVI8 and ZVI9 containing less than 3% C are mild steels, and (iii) ZVI3, direct reduced iron, containing 1.96% C belongs to the third class because of the particularity of his manufacturing technology, yielding to porous materials.

Apart from ZVI5 with a regular spherical shape, homogeneous size ($d = 1.2$ mm) and smooth surface [34], all other materials were irregular in shape (filings and shavings) with a rough surface. ZVI3 was of very rough surface and even porous. ZVI1, ZVI4, ZVI5, ZVI6 and ZVI9 were visibly covered with rust whereas all other samples retained their metallic glaze.

The nine used materials were selected from 18 Fe⁰ materials after characterization in batch experiments using the EDTA-test [15]. The results are presented elsewhere [32]. The results suggested that the batch EDTA-test may not be suitable for characterizing powdered Fe⁰ and Fe⁰ filings with high proportion of fines [32]. To test the validity of this assumption one powdered material (from six tested in Ref. [32]) was incorporated in this study together with eight materials representative for the variability of the reactivity obtained for the 12 other granular materials (chips, filings, shavings).

3.3. Iron dissolution studies

Laboratory scale glass columns were operated in up-flow mode. Nine glass columns (40 cm long, 2.6 cm inner diameter) were used. The columns were packed with sand. Each column contains 1.0 g of a different Fe⁰ material in its most upper part. The effective length, the bulk density and the porosity of the packed columns were not characterized as they were not necessary for the discussion of the results. The kinetics and the extent of iron oxidative dissolution by EDTA were the sole targets. The influent solution contained 2 mM EDTA and 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. The experiment was performed at room temperature (21–25 °C). A stable flow rate of about 11.0 mL h⁻¹ was maintained throughout the experiment. Samples for analysis were collected in flow through bottles at periodic intervals. The experiments were stopped after 62 days.

3.4. Analytical methods

The aqueous iron concentration was determined with a Varian Cary 50 UV–VIS spectrophotometer, using a wavelength of 510 nm for iron determination and following the 1,10 orthophenanthroline method [38,39]. The instrument was calibrated for iron concentration ≤ 10 mg L⁻¹. The pH value was measured by combined glass electrodes (WTW Co., Germany). Electrodes were calibrated with five standards following a multi-point calibration protocol in agreement with the current IUPAC recommendation [40].

4. Results and discussion

4.1. Expression of experimental results

The amounts of Fe dissolved during 62 days are expressed as a percentage, on a mass basis, of the total mass (1 g) of the used materials and summarized in Table 2. Although the Fe content of individual materials was available, the leaching percentage was referred to the initial mass of material (1.0 g). This choice is justified by the fact that materials are characterized on the weight basis for their capacity to be used for contaminant removal. Regardless from the actual removal mechanism, the extent of contaminant mitigation is necessarily coupled with the extent of Fe dissolution. Therefore, not the total Fe content is essential, but rather the reactive proportion (leaching extent) and the kinetics of the leaching process. The changes in pH were not recorded. The kinetics of Fe dissolution is expressed as variation of aqueous Fe concentration with the cumulative volume which is directly proportional to the elapsed time. The experiment was stopped after that 16.0–16.8 L of EDTA has flowed through the columns. Potentially, 16 L of EDTA (2 mM) can dissolve 1.8 g Fe. Depending on the electrochemical reactivity of the individual materials, the amount of leached Fe during the test varies from 27% to 73% of the initial weight of Fe⁰ material (1.0 g).

4.2. Kinetics of Fe⁰ oxidative dissolution

Fig. 1a shows that two from the nine tested materials exhibited markedly increased dissolution kinetics after the half time of the experiment (1 month corresponding to the date where 8 L of EDTA has flowed through the columns): ZVI3 (direct reduced iron) and ZVI8 (powder). After 1 month all materials exhibited very similar dissolution kinetics (Fig. 1a). The powdered material exhibited the most rapid kinetic of iron dissolution with 77% of the total leached amount of Fe (729 mg after 62 days, Table 2) been leached after

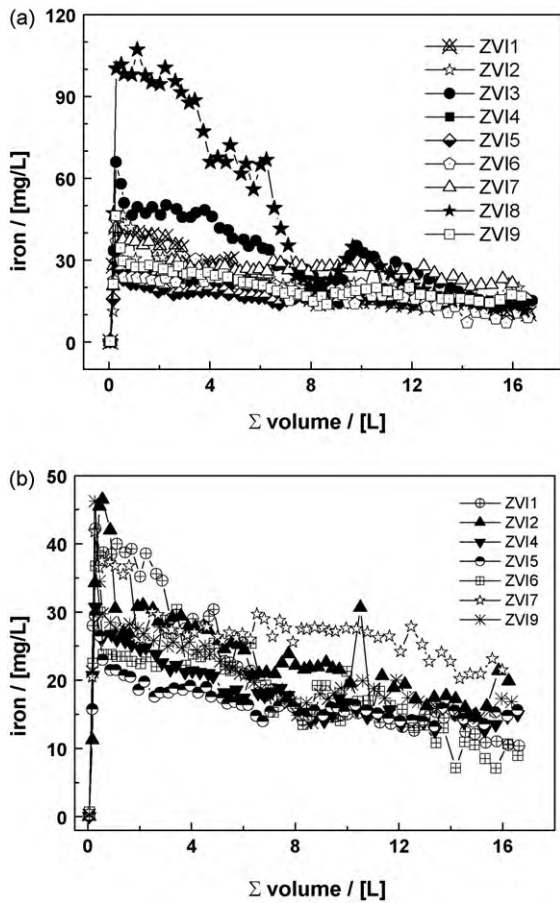


Fig. 1. Iron release (mg L^{-1}) from the Fe^0 materials by 2 mM EDTA for 62 days in column experiments: (a) all tested Fe^0 materials and (b) the seven Fe^0 materials exhibiting similar reactivity. The lines are not fitting functions, they simply connect points to facilitate visualization.

1 month. The extent of iron leaching after 1 month for all other materials, relative to the total leached amount at the end of the experiment, varies between 54% and 66%. The order of reactivity of the material deduced from the extent of leached iron after 1 month (31 days) is the following:

ZVI5 < ZVI7 < ZVI2 < ZVI9 < ZVI4 < ZVI6 < ZVI3 < ZVI1 < ZVI8.

The order of reactivity derived from the total amount of leached iron at the end of the experiment (62 days) is the following:

ZVI5 < ZVI4 < ZVI6 < ZVI9 < ZVI11 < ZVI2 < ZVI7 < ZVI3 < ZVI8.

Either Fe^0 material used in this study (including powdered ZVI8) might be suitable for use in field reactive wall applications unless it is not affordable. The different reactivity for dissolution in 2 mM EDTA would certainly influence the choice of Fe^0 with regard of site specific conditions. It is interesting to notice that ZVI9 with one of the largest surface area ($1.8 \text{ m}^2 \text{ g}^{-1}$) is one of the poorest reactive materials. Also ZVI5 and ZVI6 with the largest carbon content are among the less reactive materials. Given the similarities in surface area of used materials due to similarity in the particle size (except for powdered ZVI8 and porous ZVI3), it is definitively clear that Fe^0 manufacture history causes the observed differences in reactivity. Due to lack of information on these two aspects, their importance cannot be accurately accessed or discussed in the remainder of the paper. Although discussing the effects of Fe^0 manufacture history are over the scope of this work, a brief discussion on the impact of iron content and surface area will be given below (Table 3).

Table 3

Extent of Fe dissolution in column studies for the nine tested Fe^0 materials. ' V_T ' is the total volume of EDTA (2 mM) that has flowed into the individual columns. ' m_T ' is the total mass of leached Fe from individual materials and P (%) is the corresponding percentage relative to the initial mass of 1.0 g (or 1000 mg). As a rule, the more reactive a material the bigger the m_T and P values. General conditions: $\text{pH}_0 = 5.2$, $[\text{EDTA}]_0 = 2 \text{ mM}$, $T = 23 \pm 2^\circ \text{C}$.

Fe^0	Form	V_T (L)	m_T (mg)	P (%)
ZVI5	Spherical	16.6	272	27.2
ZVI4	Filings	16.6	295	29.5
ZVI6	Filings	16.6	298	29.8
ZVI9	Filings	16.3	332	33.2
ZVI1	Filings	16.6	340	34.0
ZVI2	Granular	16.2	376	37.6
ZVI7	Chips	16.0	430	43.0
ZVI3	Filings	16.8	513	51.3
ZVI8	Powder	16.5	729	72.9

Fig. 2 summarizes the extent of iron dissolution from tested materials as function of specific surface area (Fig. 2a) and the iron content (Fig. 2b) of the materials. It is obvious that neither the iron content nor the SSA correlated with the extent of Fe leaching by EDTA. From Fig. 2a the material with the highest surface area exhibited one of the lowest Fe leaching efficiency and from Fig. 2b the material with the lowest iron content exhibited the highest Fe leaching efficiency.

Fig. 1b summarizes the kinetics of iron dissolution from the seven granular materials (filings, chips) with similar reactivity in Fig. 1a. Due to a change in the scale on the concentration axis ($\leq 50 \text{ mg L}^{-1}$) a certain reactivity differentiation can be made graph-

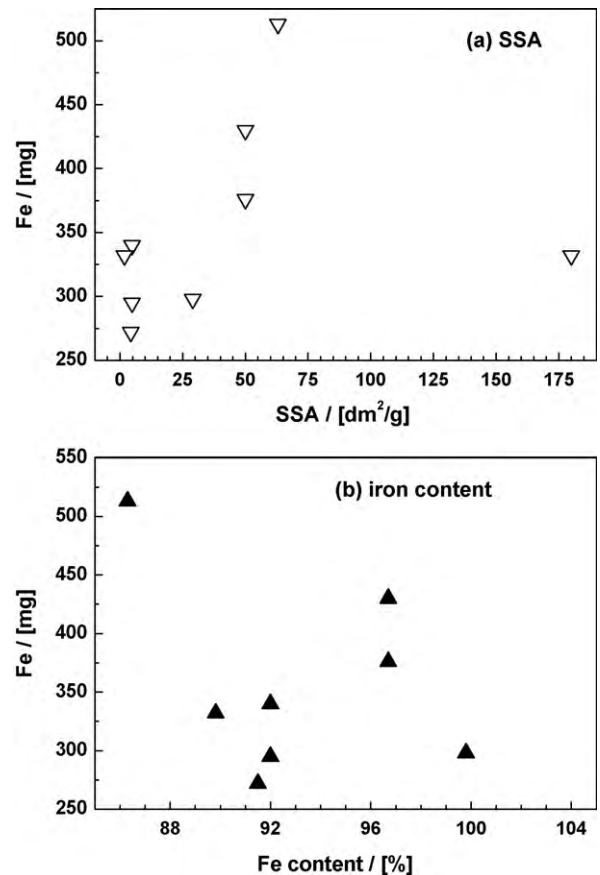


Fig. 2. Cumulative iron release (mg) from the Fe^0 materials as function of (a) material specific surface area (SSA) and (b) material iron content. It is interesting to see that both parameters play a secondary role in controlling Fe electrochemical reactivity.

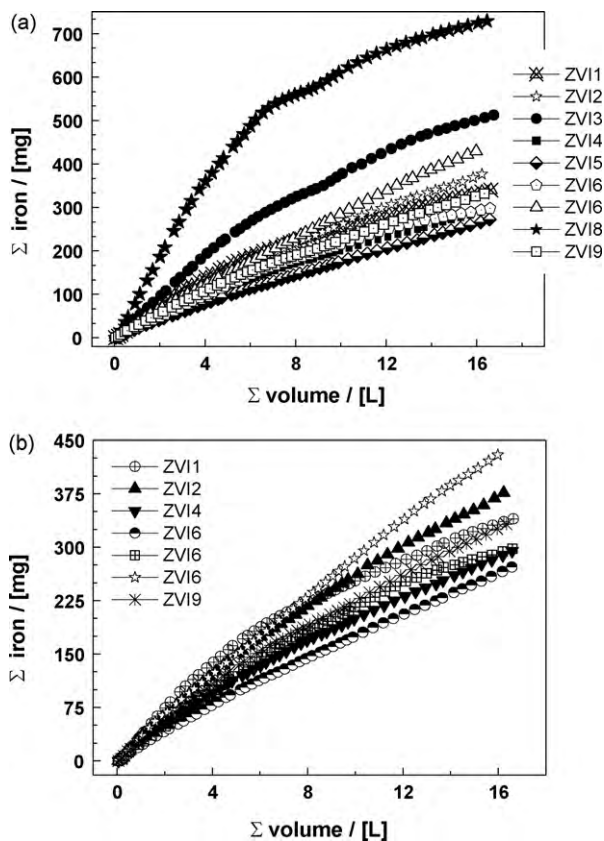


Fig. 3. Cumulative iron release (mg) from the Fe⁰ materials as function of the total volume of 2 mM EDTA passed through the columns: (a) for all tested Fe⁰ materials and (b) for the seven Fe⁰ materials exhibiting similar reactivity. The lines are not fitting functions, they simply connect points to facilitate visualization.

ically. For example it can be seen that ZVI5 (cast iron having the least surface area) is the least reactive material whereas ZVI1, ZVI2 and ZVI7 exhibit an increased initial dissolution kinetic. After about 1 month ZVI7 (and to some extent ZVI2) was the sole material exhibiting an increased dissolution kinetics. These results indicated that systems containing powdered and granulated materials will lose their efficiency sometimes after their field implementation. For systems with powdered materials the loss of efficiency is due to depletion of readily reactive site at the surface. Efficiency loss for granular material is due to intrinsic properties. Note that no passivation due to hydroxide/oxide precipitation is expected under flowing conditions in EDTA. Considering intrinsic reactivity loss in material selection will certainly reduce the probability of barrier failure. For example, Morrison et al. [41] reported on a Fe⁰/H₂O system that showed sooner breakthrough than expected for molybdenum and uranium. Performance failure was attributed to: (i) the continual build-up of mineral precipitates on the Fe⁰ surface, (ii) the loss of pore space, (iii) the development of preferential flow paths, and (iv) the complete bypass of the Fe⁰/H₂O system resulting in the loss of hydraulic control. The results of the present study suggest that a non-purposeful material selection could have been an important factor as well.

4.3. Extent of Fe⁰ oxidative dissolution

Fig. 3 summarizes the evolution of the cumulative mass of leached iron as function of the volume passed through the columns. As for the kinetics, a net difference is observed for ZVI8 and ZVI3 (Fig. 3a). All other seven materials exhibited very similar dissolution behaviour in the initial phase of the experiment (4 L of EDTA

passed or 2 weeks) and a clearer reactivity differentiation with increasing experimental duration. Most of available experiments are performed in batch systems (iron precipitation after saturation) and the experimental durations are rarely greater than 2 days. In such experiments only the initial reactivity of Fe⁰ materials are tested. Even though tested materials are often those used for field Fe⁰/H₂O systems, accurate long-term data are very difficult to obtain, particularly when service life in the range of decades are needed. This study shows that long-term column experiments (together with purposeful modelling efforts) can help to bridge the gap between field and laboratory.

5. Discussion

The results of Fe⁰ oxidative dissolution by molecular O₂ in 2 mM from this study are compared with that obtained by the same materials for methylene blue (MB) discoloration [42] and 2 mM EDTA Fe⁰ dissolution in batch systems [32]. The order of reactivity of material for column studies for 1 month (initial dissolution) and 2 months (long-term dissolution) are given separately above. The order of reactivity for the other systems are the following:

EDTA: ZVI5 < ZVI2 < ZVI9 < ZVI4 < ZVI6 < ZVI7 < ZVI3 < ZVI1 < ZVI8
 MB: ZVI5 < ZVI2 < ZVI7 < ZVI3 < ZVI6 < ZVI9 < ZVI4 < ZVI1 < ZVI8.

The comparison of the initial kinetics of Fe⁰ dissolution in batch (k_{EDTA}) and column (31 days) studies reveals that ZVI5 and ZVI2 are the least reactive materials whereas ZVI3, ZVI1 and ZVI8 are the most reactive ones. However, ZVI1, ZVI2 and ZVI5 are all cast irons whereas ZVI3 is direct reduced iron. Therefore, the relative Fe⁰ reactivity cannot be predicted from the elemental chemical composition. Only direct reduced iron could confirm the foreseeable effect of increased reactivity due to porosity or increased surface area.

The relative reactivity of the four other materials do not show also a net trend. This is certainly due to the fact that 1 month is a too long time to be considered as time of initial dissolution. Therefore, the order of reactivity considering the initial dissolution is the following obtained in batch experiments:

ZVI5 < ZVI2 < ZVI9 < ZVI4 < ZVI6 < ZVI7 < ZVI3 < ZVI1 < ZVI8.

The order of dissolution deduced from the total mass of Fe leached after 62 days was the following:

ZVI5 < ZVI4 < ZVI6 < ZVI9 < ZVI1 < ZVI2 < ZVI7 < ZVI3 < ZVI8.

It is very interesting to observe that only ZVI5 and ZVI8 conserved their ranking in both classifications. However, it can be emphasized that for longer experimental duration ZVI8 (powder) will be depleted. Therefore, the selection of a material should take into account its reactivity, the relative the flux of contaminant in the ground water and the volume of water to be treated. In some cases it could be advantageous to work with a less reactive material like ZVI5 which is reactive in the long term. Some applications will need powdered and even nano-sized Fe⁰ for short-time rapid contaminant removal. Next to the iron intrinsic reactivity yielding Fe⁰ dissolution, the relationship between Fe⁰ reactivity and contaminant removal depends on the oxide-films formed as result of iron corrosion. To take this important aspect into account the relative reactivity of used materials as accessed by the extent of methylene blue (initial concentration 20 mg L⁻¹) discoloration for 1 month [42] was compared to the data on iron dissolution in 2 mM EDTA. The results of MB removal were more comparable to that of iron dissolution in batch systems than to that of columns systems. The slight differences can be attributed to the surface state (roughness, oxidation state) of individual materials.

6. Concluding remarks

EDTA has been used for the characterization of the reactivity of Fe⁰ materials mostly of similar particle size (comparable available surface area). The observed great differences in the chemical reactivity could not be correlated with the surface area. This suggests that surface area plays a secondary role in controlling Fe⁰ electrochemical reactivity. The carbon content of the materials was not also determinant for electrochemical reactivity. Because intrinsic factors determining the chemical reactivity of Fe⁰ materials are of limited accessibility, available materials should be tested in a systematic holistic approach to identify trends in their general reactivity. In this effort, beside batch and column study with chelating agents (e.g. EDTA), long-term batch and column experiment with various contaminants are needed. Given the large spectrum of contaminants that have been successfully removed in Fe⁰/H₂O systems, this ambitious work cannot be achieved by individuals or isolated research groups. The challenge should be to move from studies proving the viability of Fe⁰ technology to investigations incorporated within a broad-based understanding of process occurring in Fe⁰/H₂O systems [43]. In this effort the proper characterization of used materials is a fundamental issue.

Acknowledgments

For providing the materials investigated in this study the author would like to express his gratitude to the branch of the MAZ (Metallaufbereitung Zwickau, Co.) in Freiberg (Germany), Gotthart Maier Metallpulver GmbH (Rheinfelden, Germany), Connelly GPM Inc. (USA), Dr. Ralf Köber from the Institute Earth Science of the University of Kiel and Dr. Vera Biermann from the Federal Institute for Materials Research and Testing (Berlin, Germany). Emin Özdem (student research assistant) is acknowledged for technical support. The work was granted by the Deutsche Forschungsgemeinschaft (DFG-No 626/2-2).

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