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Short communication

Dimensioning metallic iron beds for efficient contaminant removal

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ABSTRACT

Remediation of contaminated groundwater is an expensive and lengthy process. Permeable reactive barrier of metallic iron (Fe^0 PRB) is one of the leading technologies for groundwater remediation. One of the primary challenges for the Fe^0 PRB technology is to appropriately size the reactive barrier (length, width, Fe^0 proportion and nature of additive materials) to enable sufficient residence time for effective remediation. The size of a given Fe^0 PRB depends mostly on accurate characterization of: (i) reaction mechanisms and (ii) site-specific hydrogeologic parameters. Accordingly, the recent revision of the fundamental mechanisms of contaminant removal in Fe^0/H_2O systems requires the revision of the Fe^0 PRB dimensioning strategy. Contaminants are basically removed by adsorption, co-precipitation and size exclusion in the entire Fe^0 bed and not by chemical reduction at a moving reaction front. Principle calculations and analysis of data from all fields using water filtration on Fe^0 bed demonstrated that: (i) mixing Fe^0 and inert additives is a prerequisite for sustainability, (ii) used Fe^0 amounts must represent 30–60 vol.% of the mixture, and (iii) Fe^0 beds are deep-bed filtration systems. The major output of this study is that thicker barriers are needed for long service life. Fe^0 filters for save drinking water production should use several filters in series to achieve the treatment goal. In all cases proper material selection is an essential issue.

1. Introduction

Packed beds with metallic iron (Fe^0) are currently used as contaminant mitigating agent in several contexts including groundwater remediation, wastewater treatment and drinking water production [1–4]. Fe^0-based materials are used in particular (i) as reducing agents in permeable reactive walls [5–8], and (ii) as reagents to assist biofiltration in household filters [3,9,10]. The fundamental process responsible for contaminant removal in both contexts is necessarily the oxidative dissolution of Fe^0 (iron corrosion) which may be coupled with contaminant reduction (reactive walls) or the subsequent precipitation of iron hydroxides which may be coupled with contaminant adsorption and co-precipitation (household filters). Adsorption, co-precipitation and chemical transformations (oxidation and/or reduction) are not mutually exclusive [11–13]. It is obvious that in household filters and reactive walls, a synergy between these three processes is responsible for expected and observed decontamination. Moreover, these processes proceed in the inter-granular porosity of the packed beds which are made up of Fe^0 (100%) or a mixture of Fe^0 and an inert material (e.g. gravel, pumice, sand) [2,14]. Because of the volumetric expansive nature of the process of iron corrosion [15], the porosity of the filtrating systems certainly decreases with increasing service life, possibly yielding complete permeability loss system (filter clogging) [16,17]. The filling of the pore volume by corrosion products is necessarily coupled with improved size-exclusion capacity. Therefore, a fourth mechanism for decontamination in packed Fe^0 beds is identified.

The very recent concept that adsorption, co-precipitation and size exclusion are the fundamental mechanisms of aqueous decontamination in Fe^0 packed beds [13] is yet to be discussed in the scientific literature. The two main objectives of this communication are (i) to give some arguments supporting the new concept and (ii) to enumerate some consequences for the further development of the iron filtration technology. In this effort a particular attention is paid to filter dimensioning or bed sizing. For the sake of clarity, the presentation will start with the short history of Fe^0 for reactive walls and household filters.

2. Metallic iron for reactive walls

The Fe^0 reactive wall technology is one aspect of the materialization of the original idea of McMurty and Elton [18] that

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a passive design "using natural groundwater flow and a treatment media" can "capture or treat the contaminants without the need for regeneration or replacement". With the publication of this innovative concept in August 1985, an ongoing effort for efficient reactive materials for permeable reactive barriers started. In 1990, Gillham and his colleagues fortuitously found that corroding Fe^0 (reductively) eliminated aqueous trichloroethylene [19]. This discovery was the starting point of remediation with elemental metals. Elemental metals (e.g. Al^0, Fe^0, Zn^0 and bimetallics) are now recognized as competent alternatives for remediation of groundwater that is contaminated with reducible substances [8,20].

Currently, however, Fe^0 has exceeded all expectations because non-reducible substances have been quantitatively removed as well. For example, aqueous Zn^{II} which is thermodynamically non-reducible by Fe^0 has been efficiently removed [21]. The results of Morrison et al. [21] attested the synergic effects of removal mechanisms as the investigated systems also contained Mo^{VI} and U^{VI}. Mo^{VI} and U^{VI} could be reduced to less soluble species. Furthermore, Mo^{VI} known for its poor adsorptive capability onto iron oxides at $pH > 5$ [22,23] was quantitatively removed, suggesting that improved size exclusion might had been effective.

The concept that contaminants are fundamentally removed by adsorption and co-precipitation is consistent with many experimental observations which remained non-elucidated by the reductive transformation concept [11,12]. Although researchers are continuing to maintain the validity of the latter concept [24–26], the new concept was validated [27,28] and has been independently verified [29,30]. As a matter of course the concept of adsorption/co-precipitation (and size exclusion for packed bed) should have been challenged by researchers working on remediation in Fe^0/H_2O systems. The motivation of using Fe^0 at household level corroborates the validity of the adsorption/co-precipitation/size-exclusion concept.

3. Metallic iron for household filters

While using slow sand filtration for water treatment in rural Bangladesh, it was observed that the filter efficiency for arsenic removal depends on the iron content of natural waters. Arsenic was readily removed from Fe-rich natural waters. Accordingly, Fe^0 is used "to provide a constant input of iron (soluble or surface precipitate) for groundwater low in soluble iron" [31]. The very efficient resulting filter for As removal was the 3-Kolsi filter [10,32,33]. A typical 3-Kolsi filter contained a layer of about 3 kg Fe^0 (100% Fe^0). However, the 3-Kolsi filter was not sustainable as it clogged after some 8 weeks of operation [3,10].

The remarkable efficiency of 3-Kolsi filters has prompted researchers to further develop the system for improved sustainability [9,10,31,32,34–37]. The best product is the SONO arsenic filter in which the 100% Fe^0 layer is replaced by a proprietary porous Fe^0-based material (termed as Composite Iron Material—CIM) [32,33]. The two most important features of CIM are: (i) its porosity and (ii) its low content of Fe^0. In consequence, two opposite effects may be observed: (i) the porous structure of the CIM induces a larger reactive surface compared to non-porous Fe^0 particle (or compact Fe^0); the internal porosity could be regarded as magazine for in-situ generated iron corrosion products and (ii) less initial Fe^0 is used compared to compact Fe^0 particle. The former effect (larger reactive surface) is well-documented as tool to improve Fe^0 efficiency and is the rationale for using nano-scale Fe^0 for water treatment [38]. The latter effect (less initial Fe^0) could not improve Fe^0 efficiency in term of Fe^0 reactivity but is known as tool to delay or avoid porosity loss [39–41] of the filter system, but not the second. These observations suggest that the 100% Fe^0 layer in the 3-Kolsi filter was the major reason for its too short service life. Leupin et al. [34,35] have considerably reduced the proportion of Fe^0 (1.5 g Fe^0 for 60 g sand). More recently, Gottinger [42] demonstrated in a pilot study that a volumetric mixture Fe^0:sand of 30:70 was very efficient for water treatment at a small community level.

It is important to notice that household Fe^0 filters primarily treat water of unknown composition. Design efforts are focused on keeping filter permeability. Available filters were designed for As removal but SONO filters have efficiently removed several other chemicals and pathogens [32,43,44]. It is obvious that Fe^0-based filters regarded as "Fe^0 assisted sand filtration" are not designed to chemically reduce any contaminant. Even arsenics for which the majority of household filters were designed is removed by adsorption, co-precipitation and size exclusion, although As^V reduction to As^{III} and As^0 is thermodynamically favorable ([3,45] and references therein).

A typical SONO filter contains 5–10 kg of porous CIM (CIM: 92–94% Fe, 4–5% C, 1–2% SiO_2, 1–2% Mn, 1–2% S,P) and may function for up to 11 years while filtering waters containing up to 1000 μg As/L. It is important to notice that only a fraction of the 92–94% Fe in SONO filters is in metallic form (Fe^0) and could undergo volumetric expansion. Therefore, learning from SONO filters to design efficient Fe^0 beds consists in reducing the proportion of Fe^0 and create place for in-situ generated iron corrosion products. Prior to discuss an efficient designing tool, an overview of current design options to limit the impact of fouling in Fe^0 PRB will be given.

4. Current design approach to limit Fe^0 PRB clogging

Fe^0 PRBs are currently believed to create redox conditions for contaminant degradation or immobilization [2]. Accordingly, the precipitation of iron corrosion products and other secondary minerals is regarded as perturbing side effect yielding reactivity and porosity loss [2,14,16,17]. Accordingly, the design of a PRB requires profound knowledge of local water flow velocity (residence time), aquifer porosity, influent contaminant concentration. Additionally, the contaminant degradation rate by used Fe^0 is usually estimated in laboratory and pilot studies and used to size the PRB. Sizing aspects include the amount of Fe^0 to be used and the thickness of the bed (filter or wall). The first problem with this approach is that used Fe^0 media can not be each other compared in reactivity as there is no standard procedure to this end [46].

Recently, Li and Benson [2] identified and discussed five relevant strategies to limit the clogging of Fe^0 PRBs: (i) pea gravel equalization zones up gradient and down gradient of the reactive zone to equalize flows (strategy 1), (ii) placement of a sacrificial pretreatment zone upstream of the reactive medium (strategy 2), (iii) pH adjustment (strategy 3), (iv) use of larger Fe^0 particles (strategy 4), and (v) periodic mixing of the Fe^0 to break up and redistribute secondary minerals (strategy 5).

In the light of the concept that contaminants are basically removed by adsorption, co-precipitation and size exclusion, the following comments can be made on the five strategies. Strategy 1 necessarily has a double function as quantitative contaminant removal may occur in the equalization zones. The same remark is valid for strategy 2 as this study shows that reactive zones with 100% Fe^0 are not sustainable. Strategy 3 is recommended because iron corrosion is sustained by FeS_2 dissolution (or H^+ production). Accordingly, FeS_2 should be regarded as useful reactive additive (Fe^0/FeS_2 system or Fe^0/FeS_2/sand system). Hereby, care should be taken that the added proportion of FeS_2 do not induce a pH shift below a value of 5.5. In fact, if the final $pH < 5.5$ the Fe solubility is increased and the effluent may exhibit too high Fe concentration. On the other hand, if dissolve Fe is transported away from the reactive zone, the bed porosity will increase and the filtration efficiency will decrease. Another positively tested reactive additive is MnO_2

[29,47,48]. MnO_2 reductive dissolution is driven by Fe^{II} from Fe^0 oxidation; sustaining Fe^0 dissolution is beneficial for the decontamination process. Strategy 4 will be effective only at certain sites depending on the extent of contamination. In fact, larger size Fe^0 means larger pore space and poorer size exclusion. Finally, Strategy 5 can be rendered superfluous by a proper bed design.

The approach based on the concept that contaminants are removed by adsorption, co-precipitation and size exclusion has the advantage that only iron corrosion with site-specific water or relevant model water has to be characterized for proper barrier design. Accordingly, an aggressive groundwater will rapidly corrode iron, rendering a thin wall satisfactorily. For less aggressive waters a thicker wall is necessary to enable completed contaminant removal by multi-filtration (see Section 5.5). The same systematic can be applied to Fe^0 media of various reactivity. The less reactive a material in a groundwater, the thicker the reactive barrier. Therefore, the selection of the most appropriate Fe^0 material at each site is a key issue for wall or generally bed efficiency. The next section is focused on better designing Fe^0 beds.

5. Designing Fe^0 beds

The presentation above suggests that Fe^0 bed design must be based on the available pore volume for volumetric expansion of corroding iron. Accordingly, for a given bed size replacing a portion of reactive iron by an inert material is the first tool to extend filter service life. The very first additive material in this regard is a non-porous material as quartz (0% porosity). The next step could consist in partly or totally replacing quartz by porous materials like sandstone (up to 40% porosity) or pumice (up to 90% porosity). In each case a critical Fe^0:additive ratio must exist for which bed porosity is lost upon Fe^0 depletion as illustrated below.

5.1. Sustaining Fe^0 bed reactivity by addition of inert materials: bed design

A random packed Fe^0 bed of identical spheres is considered. The initial bed porosity Φ_0 has a fundamental value of 36% [49]. In other words, regardless from the actual dimension of the bed, 64% of the bed volume V is filled by dense Fe^0 and 36% is available as inter-granular pore space for corrosion products. It can be noticed that the compactness C of the granular medium is $C = 1 - \Phi_0 = V_{\text{initial Fe}}/V = 0.64$ where $V_{\text{initial Fe}}$ is the initial volume of iron. If a volumetric fraction of Fe^0 is replaced by non-porous quartz (with the same particle diameter), 36% of the bed volume is still available for corrosion products but more Fe^0 will corrode before the bed porosity decreases to zero (Fig. 1). Calculations could enable the identification of critical Fe^0:additive ratios. Two hypothetical examples will be used here for illustration: (i) a rectangular reactive wall and (ii) a cylindrical household filter.

The dimensions of the demonstration reactive wall in Borden (Ontario, Canada) are used for the hypothetical reactive wall [5]. The dimensions of the wall were 5.5 m × 1.6 m × 2.2 m ($l \times w \times h$), giving a volume $V = 19.36\,\text{m}^3$. For the hypothetical cylindrical household filter the dimensions of field columns used by Westerhoff and James [50] are adopted. The columns had a total capacity or volume $V = 4.022 \times 10^{-3}\,\text{m}^3$ (4.022 L): diameter 7.5 cm and height 91 cm.

The filling of the bed porosity by iron corrosion products can be estimated from a simplified modeling (Fig. 1) based on the following assumptions:

(i) uniform corrosion: the diameter reduction of the particle is the same for all the Fe^0 particles,
(ii) iron corrosion products are fluid enough to progressively fill available pore space.

Assuming that the coefficient of volumetric expansion (η) of the iron corrosion products is:

$$\eta = \frac{V_{\text{oxides}}}{V_{\text{Fe}}} \tag{1}$$

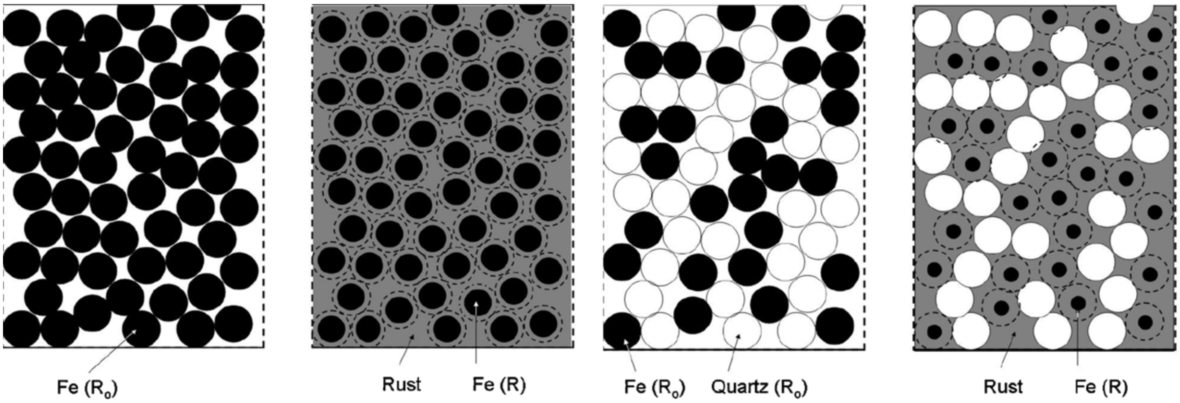
where V_{oxides} is the volume of the iron corrosion products and V_{Fe} the volume of parent Fe^0. The surplus volume of the iron corrosion products contributing to porosity loss is V'_{oxides}. Per definition V'_{oxides} is the difference between the volume V_{oxides} of iron corrosion products and the volume V_{Fe} of parent Fe^0. V'_{oxides} is given by Eq. (2):

$$V'_{\text{oxides}} = (\eta - 1) \times V_{\text{Fe}} \tag{2}$$

Assuming that the bed is clogged when the volume V'_{oxides} is equal to the initial inter-granular voids ($\Phi_0 \cdot V$), the volume $V_{\text{Fe, clogging}}$ of the consumed iron leading to clogging of the bed is then estimated by:

$$V_{\text{Fe, clogging}} = \frac{\Phi_0 \cdot V}{\eta - 1} \tag{3}$$

In this case (Eq. (3)), the volume $V_{\text{Fe, clogging}}$ of the consumed iron is inferior to the initial volume of dense Fe^0. It means that clogging appears before depletion of Fe. It can be noticed that, in some cases, the initial volume of iron may be too low so that there is no clogging and the bed porosity is not completely filled by iron corrosion products.



(a) volumetric ratio Fe^0:quartz 100:0

(b) volumetric ratio Fe^0:quartz 50:50

Fig. 1. Schematic illustration of the impact of mixing Fe^0 and quartz for the long-term reactivity of Fe^0 beds (clogging). When Fe^0 is mixed with quartz more iron corrodes and the initial porosity is progressively filled with porous iron oxides for water multi-filtration.

Table 1
Mass of material necessary to completely fill the hypothetical treatment units with 100% metallic iron. The fundamental porosity of $\Phi_0 = 36\%$ is assumed and the value of 7800 kg/m^3 is taken for the specific weight of Fe^0.

Unit	V_{unit} (m^3)	V_{Fe} (m^3)	V_{pores} (m^3)	m_{Fe} (kg)
Filter	0.004	0.0026	0.0014	20.08
Wall	19.4	12.4	6.97	96,645

The residual porosity Φ_r defined by $\Phi_r = V_{residual\ voids}/V$ is evaluated by Eq. (4):

$$\Phi_r = \Phi_0 - (\eta - 1).\frac{V_{consumedFe}}{V} \tag{4}$$

where $V_{consumedFe}$ is the volume of Fe which is consumed. When the clogging appears before depletion of Fe^0, the volume $V_{consumedFe}$ is given by Eq. (3) and the residual porosity is equal to $\Phi_r = 0$. When there is no clogging, the volume $V_{consumedFe}$ is equal to the initial volume of Fe and there is residual porosity ($\Phi_r \neq 0$).

These calculations allow the evaluation of the efficiency of the bed (reactive wall or filter) related to the possible clogging. Two cases are discussed in the following.

5.2. *Case of a 100% Fe^0 bed*

Considering that the density of Fe^0 is 7800 kg/m^3, the 12.4 m^3 (64% of the total volume) available in the hypothetical reactive wall (Table 1) can be filled by 96,645 kg of Fe^0. The calculations in Table 2 demonstrated that from this Fe^0 amount only a maximum of 50,336 kg can be oxidized to yield porosity loss (no residual porosity, $\Phi_r = 0$). The weight proportion of consumed Fe^0 ranges between 10.4% and 52.1% when the main corrosion products are $Fe(OH)_3{\cdot}3H_2O$ (ferrihydrite) or Fe_2O_3 (hematite), respectively, showing that 100% Fe^0 reactive walls are pure material wastage. The calculations for the hypothetical household filter demonstrated that only 2.1–10.5 kg of Fe^0 will be consumed corresponding to the same weight percent like for the hypothetical reactive wall.

Ideally, when Fe^0 is mixed with quartz, a bed containing more than 52.1 wt.% Fe^0 of the mass of Fe^0 necessary to have a 100% Fe^0 bed should not be constructed because bed clogging will happen and excess Fe^0 will not react (material wastage). The actual Fe^0 proportion will depend on its intrinsic reactivity and the kinetics of iron oxidative dissolution. Kinetics aspects are not considered in this study.

5.3. *Case of a volumetric Fe^0:quartz ratio of 50:50*

The calculations above suggests that only about 10.4–52.1 wt.% Fe^0 is necessary to fill the pore space of a 100% Fe^0 filter regardless from the bed dimensions. In this section, the calculations are made for a volumetric Fe^0:quartz ratio of 50:50. To calculate the corresponding weight ratio, one should use the particle size and the densities. However, because the same beds (wall and filter) are used, the bed volume occupied by 50 vol.% is necessarily one half of the value used in the pure Fe^0 bed: (i) 6.20 m^3 or 48,322 kg for the wall and (ii) 1.3×10^{-3} m^3 (1.3 L) or 10.4 kg for the filter. It is evident that the Fe^0 masses consumed to yield bed clogging are the same as in the 100% Fe^0 case. The percent consumption is then higher (more iron is consumed to obtain the same volume of iron corrosion products at Fe^0 depletion, Fig. 1) and varies from 21% for $Fe(OH)_3{\cdot}3H_2O$ to 100% for Fe_2O_3 and Fe_3O_4.

Table 2
Mass (m_{wall} or m_{filter} in kg) of iron and weight proportion of consumed iron (P in %, same value for the wall or the filter) leading to porosity loss in the hypothetical field reactive wall and household filter as function of the nature of corrosion products. Φ_r is the residual porosity (in this case $\Phi_r = 0$ and iron is not completely consumed, $P < 100\%$). V_{oxid}/V_{Fe} values are expansive coefficients from Ref. [15].

Oxid	V_{oxid}/V_{Fe}	m_{wall} (kg)	m_{filter} (kg)	P (%)	Φ_r (%)
1/2 Fe_2O_3	2.08	50,336	10.45	52.1	0
1/3 Fe_3O_4	2.12	48,538	10.08	50.2	0
γ-FeOOH	3.03	26,779	5.56	27.7	0
β-FeOOH	3.48	21,920	4.55	22.7	0
$Fe(OH)_2$	3.75	19,768	4.11	20.5	0
α-FeOOH	3.91	18,681	3.88	19.3	0
$Fe(OH)_3$	4.2	16,988	3.53	17.6	0
$Fe(OH)_3{\cdot}3H_2O$	6.4	10,067	2.09	10.4	0

Table 3
Weight proportion P of consumed iron leading to porosity loss (Eq. (3)) or residual porosity Φ_r (Eq. (4)) as function of the nature of corrosion products for Fe^0:sandstone with a volumetric ratio 50:50. V_{oxid}/V_{Fe} values are expansive coefficient from Ref. [15]. The critical porosity of sandstone is 40% and its specific weight is 2.0 kg/m^3. The results are the same for the reactive wall and the household filter.

Oxid	V_{oxid}/V_{Fe}	P (%)	Φ_r (%)
1/2 Fe_2O_3	2.08	100	14.2
1/3 Fe_3O_4	2.12	100	12.9
γ-FeOOH	3.03	75.1	0
β-FeOOH	3.48	61.5	0
$Fe(OH)_2$	3.75	55.5	0
α-FeOOH	3.91	52.4	0
$Fe(OH)_3$	4.2	47.7	0
$Fe(OH)_3{\cdot}3H_2O$	6.4	28.2	0

The bed containing 50 vol.% Fe^0 is necessarily clogged at Fe^0 depletion; no residual porosity ($\Phi_r = 0$). However, an ideal treatment system should keep a certain residual porosity. This is particularly important for subsurface reactive barriers. To warrant a residual porosity ($\Phi_r \neq 0$) while using a constant Fe^0 amount in the bed, it appears that thicker beds have to be considered. For example the amount of additive material can be increased such that the resulting volumetric proportion of Fe^0 is 35%. Another tool to sustain Fe^0 reactivity is to use porous additive instead of non-porous quartz. In this way, the total volume for the storage of in-situ generated iron corrosion products is increased and the residual bed porosity at Fe^0 depletion is warranted as will be illustrated in the next section.

5.4. *Lengthening Fe^0 bed service life by porous additives*

When quartz particles from Section 5.3 are replaced by V_{PP} of porous particles (with $V_{PP} = V - V_{initial\ Fe}$), the available porosity Φ'_0 for iron corrosion products is increased according to:

$$\Phi'_0 = \Phi_0 + \varphi_{pp} \cdot f_{pp} \tag{5}$$

where φ_{pp} (–) is the critical porosity of the porous particles; f_{pp} (–) is the porous particle volume fraction (here $f_{pp} = V_{PP}/V$).

The volume V_{Fe} of the consumed iron leading to clogging of the bed (Eq. (3)) or the residual porosity Φ_r (Eq. (4)) can be obtained by replacing Φ_0 by Φ'_0. The calculations in Table 3 show that it is possible to increase the efficiency of the filtration system. More iron may be consumed and transformed into iron corrosion products before clogging. In two cases (Fe_2O_3 and Fe_3O_4), a residual bed porosity is available at Fe depletion.

Fig. 2 shows that replacing quartz by sandstone or more porous (or less dense) materials could further extend Fe^0 bed service life. This conclusion is justified by the fact that heavier materials are less porous. However, the most important feature from Fig. 2 is that weight-based and volumetric ratios are not linearly dependent. Therefore, the description of any experimental design should comprise data on Fe^0 and additives (form, density, porosity, size) and filter dimensions together with the volumetric proportion of Fe^0. This procedure will enable or ease comparability of published results.

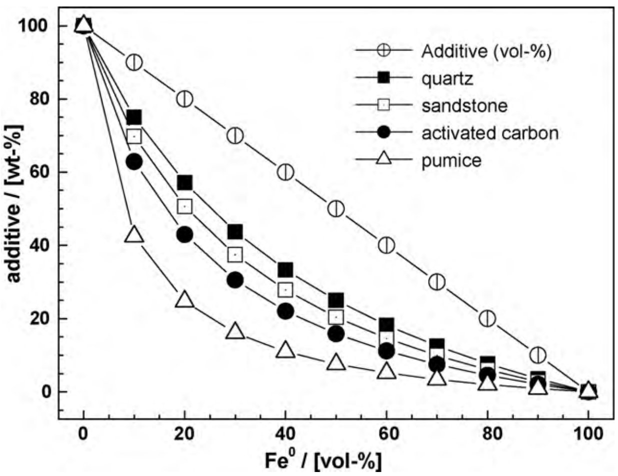


Fig. 2. Variation of the weight percent of additive materials as function of the Fe^0 volumetric ratio. Due to the differences in density, there is no linear dependence. The depicted variation of the wt.-ratio depends on the material density. Used density values are: Fe^0: 7.80 g/cm^3, quartz: 2.65 g/cm^3, sandstone: 2.00 g/cm^3, activated carbon: 1.47 g/cm^3, and pumice 0.64 g/cm^3.

5.5. Discussion

The calculations above have shown that in a 100% Fe^0 bed, system clogging will occur when only about 52 wt.% of used Fe^0 is consumed. In a 50% Fe^0 bed material depletion (100% consumption) is only possible if the corrosion products are Fe_3O_4 and Fe_2O_3 (no residual porosity). By replacing quartz by sandstone, a residual porosity Φ_r about 12% is obtained when the corrosion products are Fe_3O_4 and Fe_2O_3. But even in these cases, crystalline Fe_3O_4 and Fe_2O_3 are the final stages of transformations which go through several more volumetric amorphous stages (e.g. $Fe(OH)_2$, FeOOH). Accordingly, a volumetric ratio 50:50 should be regarded as the highest proportion of Fe^0 for long-term efficiency of Fe^0 beds. In the literature however, a 50:50 weight ratio is usually used based on a pragmatic approach [50]. The volumetric 50:50 ratio for the Fe^0:quartz mixture (quartz: 2.6 kg/m^3) corresponds to a Fe^0:quartz weight ratio of 75:25. The suitability of the volumetric ratio in this context arises from the fact that the expansive nature of iron corrosion is to be considered. Finally, a consideration of the conditions used by O'Hannesin and Gillham [5] and Westerhoff and James [50] is made.

O'Hannesin and Gillham [5] used only 22 wt.% Fe^0 in the reactive wall in Borden (Ontario Canada). This proportion corresponds to less than 10 vol.% Fe^0 showing that the demonstration wall at Borden is highly permeable. Accordingly, system clogging due to expansive iron corrosion is not expected because the available pore space is by far larger than the volume of iron corrosion products at Fe^0 depletion. As discussed in Section 4, most Fe^0 PRBs content a zone with 100% Fe^0. In some cases "equalization zones" and a "sacrificial pre-treatment zone" exist in which Fe^0 is mixed with gravel or sand. In recent barriers mixing Fe^0 and sand is considered as a tool to save expense for Fe^0 media [51]. However, the proper consideration of the expansive nature of Fe^0 corrosion shows that mixing Fe^0 and inert material is a prerequisite for long service life.

Westerhoff and James [50] could evidence the difficulty of performing long-term experiment with 100% Fe^0 beds. A weight-base 50:50 Fe^0:sand bed could perform accurately for several months (12 months). Similarly, household 100% Fe^0 filters were abandoned because of rapid clogging [10,32]. The calculations above rationalize the current renaissance of Fe^0 filter technology for household filters [52] and its use for small scale water facilities [42,53]. Fe^0 filter technology is regarded as a flexible and affordable technology, which could enable the achievement of the Millenium Development Goals (MDGs) for water. This simple technology could even enable to achieve universal access to safe drinking water within some few years [52].

6. General discussion

6.1. Fe^0 bed as adsorptive size-exclusion system

The consideration of Fe^0 beds as adsorptive size-exclusion systems arises from the strong adsorptive properties of in-situ generated iron corrosion products [54]. Iron is progressively corroded (uniform corrosion) in the whole bed. Contaminants are removed by adsorption, co-precipitation and size exclusion within the whole bed. Removed contaminants could be further chemically transformed (oxidized or reduced). A contaminant that is not removed in the entrance zone could be removed deeper in the Fe^0 bed (deep-bed filtration). This behaviour is illustrated the best by simple experiments by Leupin and Hug [34]. These authors performed an As removal experiment in a series of four filters. Each filter contained 1.5 g iron and 60 g sand. The system with a total of 6 g iron could efficiently filtered 36 L of an aqueous solution containing 500 mg As/L. A close consideration of the filtration efficacy pro filtration event showed that less than 20% (100 mg As/L) of the initial arsenic was removed during the first filtration; a much larger fraction ($\geq$200 mg As/L) was removed during the second filtration, arsenic removal continued during the third and fourth filtration. It is important to note that Fe^0 was not depleted in the experiments and the filters were not clogged. Accordingly, further As removal occurred even though As breakthrough ([As] > 50 µg/L) was observed. The Fe^0 weight percent of 2.4 was necessarily too low for efficient filtration in a single event, but has the advantage to avoid the clogging of the filter. However, this experiment demonstrated the deep-bed filtration nature of individual Fe^0 beds which could equally be demonstrated with four sample ports on a single bed.

For the further illustration of deep-bed filtration nature of Fe^0 beds, Fig. 3 compares the breakthrough of contaminants in a granular activated carbon (GAC) bed and a Fe^0 bed. To be treated, water is applied directly to the upper end and allows to flow through the packing bed by gravity.

GAC is inert in water and the adsorption capacity is consumed only by contaminants which displace H_2O from adsorption sites. Accordingly, the region where contaminant adsorption takes place is called the mass-transfer zone (or adsorption front). The region above the adsorption front is the saturated zone and the region below is the virgin zone. As a function of time, the saturated zone moves through the bed and approaches the end [55]. The adsorption bed is exhausted when no more satisfactorily decontamination is achieved.

On the contrary, in a Fe^0 bed, the whole bed is available as sorption, co-precipitation and size-exclusion system. A sort of "adsorption front" may exist because of increased oxidizing agent's levels in the inflowing solution. However in the whole bed H_2O corrodes Fe^0 producing corrosion products for efficiency contaminant removal. Contaminant removal may thus occur deeper in the Fe^0 bed from the initial stage of bed service on.

6.2. Significance for system design

The scientific community has long been searching for common underlying mechanisms for the process of contaminant removal in Fe^0/H_2O systems that provide a confidence for design that is non-site-specific [56,57]. This was the idea behind introducing specific reaction rate constant (k_{SA}). k_{SA} values are regarded as a more general reactivity descriptor of contaminants with Fe^0. They are also

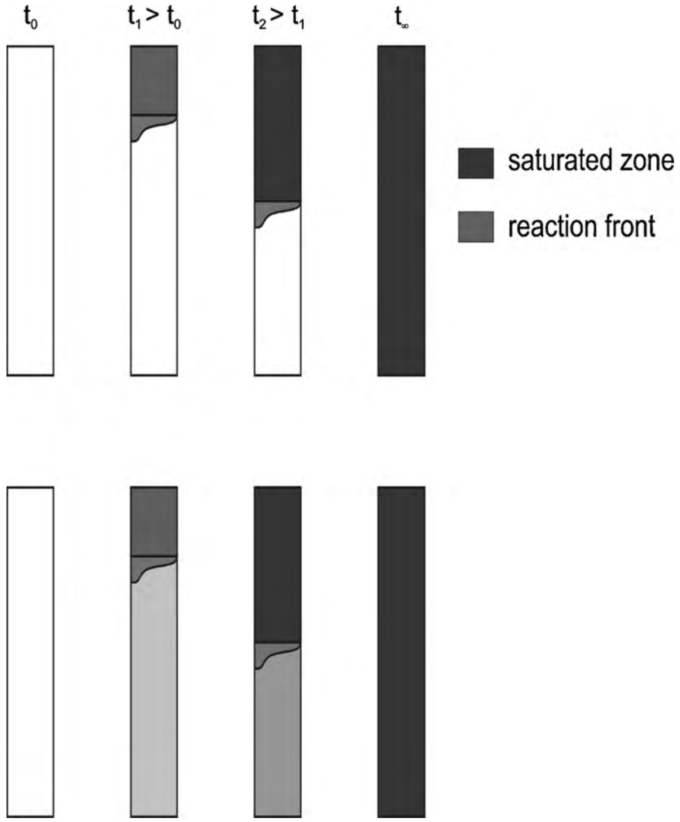


Fig. 3. Comparison of the evolution of contaminant loading in granular activated carbon (GAC—up) and Fe^0 (down) filters. The evolution of the GAC filters is virgin—preloaded (reaction front) and saturated carbon. For the Fe^0 filters a reaction front may exist due to increased O_2 in the influent but iron corrosion by H_2O (or H^+) occurs uniformly in the whole column. The light grey shadow indicates progressive Fe^0 corrosion by water.

believed to allow intersystem comparisons [57]. However, there are two major problems with the k_{SA} concept: (i) it is contaminant specific and (ii) it is based on the concept of reductive transformation which is definitively not determinant for the process of the removal of several contaminants.

While previous efforts were directed at achieving a significant body of removal rate for individual contaminants in order to enable non-site-specific bed design, the present study suggests that site-specificity will govern material selection. For example, if contaminated water is carbonate-rich, it could be advantageous to use a relative low reactive material which corrodibility will be sustained by carbonates. Accordingly, if available Fe^0 is classified for specific conditions, treatability studies may only be required to fine-tune design criteria for the optimal Fe^0 bed performance.

7. Concluding remarks

This study clearly delineates the important role of volumetric expansion of corroding iron for the process of contaminant removal in Fe^0 beds and the sustainability of Fe^0 beds. Sustainability is primarily warrant by admixing Fe^0 with non-reactive additives to avoid or delay porosity loss. The characterization of Fe^0 beds by the volumetric Fe^0:additive ratios and the bed sizes provide a clear starting point for the design of future laboratory, pilot, and field-scale studies aiming at characterizing remediation Fe^0 beds. This certainly has economic implications for Fe^0 bed design as the use of too high Fe^0 amount (e.g. >60 vol.%) has to be avoided. Most importantly results will be more comparable, accelerating progress in technology development.

The most important result from the calculations of this study is that, for a given Fe^0 amount, necessary for efficient decontamination at a specific contaminated site, building a thicker barrier in which iron represents a volumetric proportion of 30–45% is more advantageous than a thin barrier containing more than 60 vol.% iron. A further useful tool to extend Fe^0 bed service live is to use porous additives which allow avoiding/delaying bed clogging.

The installation of thicker reactive walls in the underground is certainly coupled with elevated investment costs. However, thickening the barrier is essential for barrier sustainability (deep-bed filtration). For household filters and Fe^0 beds in water treatment plants [42,53] the achievement of multi-filtration is an easier task as for instance, several beds could let to operate in series.

Finally, it should be highlighted that the very first reactive wall constructed at Borden (Ontario, Canada) for the demonstration of the feasibility of the new technology contained less that 10 vol.% (Fe^0) and could never been clogged because the porosity of the system could not be filled by expansive iron corrosion products. In other words because of insufficient system analysis, the Fe^0 reactive wall technology was demonstrated on a very permeable system but operating walls are necessarily less permeable. Moreover, mixing Fe^0 and sand was considered as a tool to reduced Fe^0 costs [41,51]. It is now demonstrated, that mixing Fe^0 with inert additives is even the prerequisite for sustainability. It is hoped that the huge literature on deep-bed filtration [58–60] will now be used for the further development of iron wall technology.

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