

# Optimising the Design of Fe<sup>0</sup>-Based Filtration Systems for Water Treatment: The Suitability of Porous Iron Composites

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**Abstract:** This study assessed the functionality of metallic iron (Fe<sup>0</sup>) filtration systems using porous iron composite (PIC) as an alternative to granular Fe<sup>0</sup>/aggregate mixtures. The usage of PIC for water treatment has many challenges which are related to the well-drained nature of highly porous filters and the corresponding increase in hydraulic conductivity (shorter contact time). In this article, the extent of (i) iron exhaustion and (ii) porosity loss in four filtration systems are critically discussed. The considered filtration systems are: (i) Fe<sup>0</sup> alone, (ii) PIC alone, (iii) Fe<sup>0</sup>/sand and (iv) Fe<sup>0</sup>/pumice. In all four systems, mono-sized granular spherical particles are assumed. Sand and Fe<sup>0</sup> are compact ( $\phi = 0\%$ ) whereas PIC and pumice are porous (e.g.  $\phi = 40\%$ ). Results demonstrated that under anoxic conditions (Fe<sub>3</sub>O<sub>4</sub> as major corrosion products) Fe<sup>0</sup> depletion is possible in all systems except Fe<sup>0</sup> alone. Under oxic conditions (e.g. formation of Fe(OH)<sub>3</sub>), the PIC system exhibited the highest level of Fe<sup>0</sup> depletion (58%). The increasing order of sustainability was: Fe<sup>0</sup> < Fe<sup>0</sup>/sand < Fe<sup>0</sup>/PM < PIC. These results suggested that manufacturing PIC with defined porosity and intrinsic reactivity is the key for more efficient usage of Fe<sup>0</sup> for environmental remediation and water treatment.

**Keywords:** Porous media, Permeability loss, Reactive filtration, Water treatment, Zero-valent iron.

## 1. INTRODUCTION

The suitability of metallic iron (Fe<sup>0</sup>) for water treatment has motivated a great deal of work on the development of Fe<sup>0</sup>-based filtration systems during the past two decades [1-19]. Within the remediation community, metallic iron is commonly termed as zero-valent iron (ZVI). Fe<sup>0</sup>-based filtration has been demonstrated an affordable, applicable and efficient water treatment system. Fe<sup>0</sup> has been successfully used in environmental remediation during the past two decades [3,11,13,20-22]. There are currently more than 200 subsurface Fe<sup>0</sup>-based permeable reactive barriers (Fe<sup>0</sup> PRBs) installed worldwide [11,16]. Despite the large volume of work done on 'using Fe<sup>0</sup> for environmental remediation', progress towards the understanding of involved processes is slow. Recent progress in understanding the operating mode of Fe<sup>0</sup> filtration systems has revolutionized the design of

Fe<sup>0</sup>-based filters for safe drinking water provision and wastewater treatment [10,16,18,23-33]. The achieved progresses are mainly based on theoretical considerations [8,23,27,34-39].

There is a broad consensus in the technical literature that Fe<sup>0</sup> is a reducing agent under experimental conditions [3,12]. However, there is little agreement on the interpretation of experimental data on all the pertinent variables which have decisive influence on the reduction process. Also, because primary Fe<sup>0</sup> oxidation products (Fe<sup>II</sup> and H/H<sub>2</sub>) are reducing agents, the reactions investigated are inherently complex [18, 34-37]. The complexity of the Fe<sup>0</sup>/H<sub>2</sub>O system has exacerbated the search for Fe<sup>0</sup> filter designs that provide sustainable water treatment with low maintenance [40-44]. The significant importance of admixing granular compact Fe<sup>0</sup> with non expansive materials (e.g. gravel, MnO<sub>2</sub>, pumice, sand) has recently been demonstrated [37,38,45-51]. The usage of porous, non-expansive materials (e.g. anthracite, pumice) as admixing agents for Fe<sup>0</sup> was experimentally demonstrated beneficial for filter's

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sustainability [15,32,52-54]. The sustainability characteristic was attributed to the availability of intra-particular spaces (pores) within pumice particles for storage of in-situ generated iron corrosion products [54]. However, in comparison to  $\text{Fe}^0$ /sand systems, more permeable  $\text{Fe}^0$ /pumice systems were less efficient for contaminant removal [32]. This observation demonstrated the crucial challenge of concealing two controversial issues in designing sustainable  $\text{Fe}^0$  filters: (i) increased contaminant removal efficiency (as much  $\text{Fe}^0$  as possible) and (ii) increased system permeability (as less  $\text{Fe}^0$  as possible). The introduction of a  $\text{Fe}^0$ -based porous composite (termed composite iron matrix - CIM) as reactive material [6,17,55-57] in a sustainable filter (SONO filter) suggests that  $\text{Fe}^0$ -based porous composites should be regarded as the next generation filter materials.

Another CIM-like material termed as SIM (sulfur-modified iron) has been recently presented by Allred [10,24,25] as reactive material in filters for agricultural drainage water treatment. Direct reduced iron (DRI or ‘sponge iron’) was also tested as an alternative to conventional compact Fe<sup>0</sup> for wastewater treatment [19, 58-64]. DRI results from direct reduction of iron ore by a reducing gas produced from natural gas or coal [64]. DRI resembles a honey comb structure and is spongy in texture. DRI may react differently in many ways when compared to compact iron ( $\phi = 0$ ). Inherent characteristics of DRI are high porosity ( $\phi \neq 0$ ), low density and high surface area. Sponge iron is a traditional water treatment material [65-67], but its application in passive filters is regarded as a new research field. For example, the ‘sponge iron’ tested by Yi *et al.* [19] is a commercial material which is conventionally used as oxygen scavenger for water treatment. This material exhibits a density of 2.2 g/cm<sup>3</sup> and a specific surface area of 85 m<sup>2</sup>/g. In essence, conventional DRI can be properly micro-alloyed to

manufacture various CIM-like materials. It should be noticed that the original CIM material is a porous matrix produced by in-situ processing inside the filter. The starting materials termed as CIG (composite iron granules) have a porosity ranges between 8 % and 20 % [56]. In this article, all porous CIM-like materials are collectively termed as PIC (Table 1).

This article applies a theoretical approach to discuss the suitability of PIC on the performance of  $\text{Fe}^0$  filters. The sustainability of  $\text{Fe}^0$ , PIC,  $\text{Fe}^0/\text{sand}$  and  $\text{Fe}^0/\text{pumice}$  systems are comparatively discussed. Systems are compared in terms of (i) the extent of  $\text{Fe}^0$  exhaustion and (ii) the extent of porosity loss.

## 2. FUNDAMENTAL ASPECTS OF CLOGGING OF GRANULAR Fe<sup>0</sup> FILTERS

Gradual decrease of the hydraulic conductivity (permeability loss) of granular Fe<sup>0</sup> filters as water passes through them has been intensively investigated during the last two decades [1,3,11,20-22,44,68-71]. The reason for the permeability loss is certainly the deposition of precipitates in the voids between granular Fe<sup>0</sup> particles (inter-granular porosity). However, a comparative performance analysis of published data is almost impossible because important media characteristics such as shape, surface smoothness and Fe<sup>0</sup> intrinsic reactivity have not been well documented or were documented in a limited way [15,30,32,33]. Moreover, the crucial importance of the expansive nature of iron corrosion [72-74] to fill the initial porosity was not properly considered [38,39,45-51]. Accordingly, it is important to consider 'endogen' causes (e.g. grain's shape and surface smoothness, porosity of grains, changes in size of Fe<sup>0</sup> grains, nature of packing arrangement) for clogging of granular Fe<sup>0</sup> filters in more details. Only once these 'endogen' parameters are properly considered, an accurate evaluation of the impacts of external factors (e.g.

**Table 1:** Some characteristics of two compact Fe<sup>0</sup> and three selected porous iron composites from the literature. The paucity of data relevant for proper discussion on Fe<sup>0</sup> reactivity is obvious. The characteristics of the PIC (SMI) introduced by Allred [10,24,25] are not specified. n.s. stands for not specified

precipitation of foreign species including  $\text{CaCO}_3$  and  $\text{FeCO}_3$ ) would be adequate.

Despite two decades of intensive researches on granular  $\text{Fe}^0$  filters for water treatment, limited works have been done to understand filter clogging phenomenon as impacted by expansive iron corrosion [15,32,45-54]. The inter-relationship between permeability loss and treatment performance has been mostly investigated on a pragmatic basis. Many researches performed 'with sufficient  $\text{Fe}^0$  to remove all of the aqueous contaminants' until/before system clogging. Evidently this approach is less useful when it comes to search for generalized design criteria like optimal filter depth or  $\text{Fe}^0$  ratio in a reactive zone. As an example, the following volumetric (v/v) or weight (w/w)  $\text{Fe}^0$ :sand ratios were tested by various investigators such as: 22:78 (w/w) [3], 50:50 (w/w) [29,66], 15:85 (v/v) [31]. The question arises how to compare such results where each study targeted on different contaminants while using columns of different dimensions.

Recently, it has been demonstrated that using small  $\text{Fe}^0$  quantities in laboratory columns would enable the characterization of involved processes within a reasonable experimental time (up to 4 months) [30,33,75-77]. In such type of experiments, the goal is not 'no breakthrough', but rather the characterization of  $\text{Fe}^0$  reactivity and the resulting efficiency of the reactive system despite breakthrough. The results of such experiments could be 'transposed' to cases where a tolerable level of contamination is needed. Additionally, these systems give a realistic image of the kinetics of

iron corrosion over the initial stage of increased reactivity. This 'residual reactivity stage' is a key stage to assess if reliable results for long term performance prediction are sought.

The present study comparatively characterizes the evolution of the porosity in four  $\text{Fe}^0$ -based filtration systems as  $\text{Fe}^0$  is progressively consumed at the 'residual reactivity stage'. It is certain that compact  $\text{Fe}^0$  and (porous) PIC will corrode under different kinetics but these kinetic aspects are not addressed here.

### 3. THE PROCESS OF POROSITY LOSS IN VARIOUS $\text{Fe}^0$ FILTERS

In this section, an evaluation of porosity loss in a series of four  $\text{Fe}^0$  filters is given. The four reactive systems are: (b) 'Fe<sup>0</sup> alone', (d) 'PIC alone', (e) 'Fe<sup>0</sup>/sand' and (f) 'Fe<sup>0</sup>/PM' (Figure 1). Two mono-aggregate systems ((a) 'sand alone' and (c) 'pumice alone') are considered as operational references.

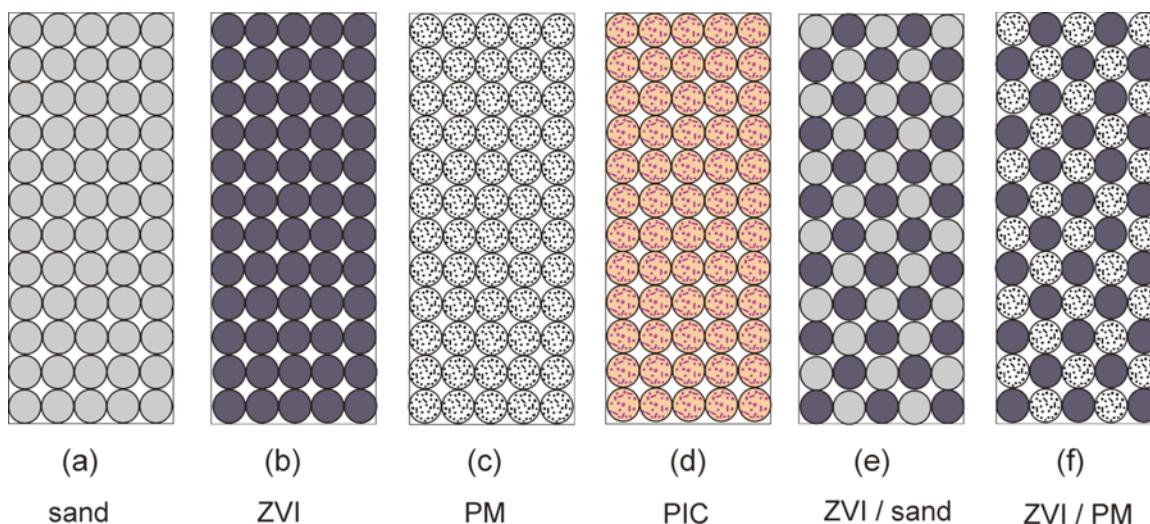
#### 3.1. Equation of the Filters

The equations of  $\text{Fe}^0$  filters have been recently established [38,47,48,51]. These equations are based on the volumetric fraction of voids (pores) in a filter and its evolution with time. The fundamental equations are:

$$V_{\text{solid}}^0 + V_{\text{pore}}^0 = V_{\text{filter}} \quad (1)$$

$$\alpha_{\text{solid}} + \alpha_{\text{pore}} = 1 \quad (2)$$

Where  $V_{\text{solid}}^0$  is the volume occupied by compact (non porous) solid particles,  $V_{\text{pore}}^0$  the volume of the



**Figure 1:** Schematic layout of the six systems discussed in this study. All particles are assumed spherical, the resulting columns are of similar compactness. The initial inter-granular porosity ( $V_{\text{pore}}^0$ ) is the same for all the systems. Considered materials are: sand (compact), metallic iron (ZVI - compact), pumice (PM - porous), and porous iron composite (PIC).

inter-granular voids, and  $V_{\text{filter}}$  the total volume of the filter (or a reactive zone within a filter).  $\alpha_{\text{solid}}$  and  $\alpha_{\text{pore}}$  are the corresponding volumetric fractions.

Per definition,  $\alpha_{\text{solid}} = C$  is the compaction coefficient (compactness) and  $\alpha_{\text{pore}} = \Phi_0 = 1 - C$  is the initial porosity. For a centred cubic arrangement of compact (non porous) spherical particles,  $C = 0.64$  and  $\Phi_0 = 0.36$ . These ideal values will be considered during the estimations of this study. For porous particles with an internal porosity  $\phi$ ,  $V_{\text{solid}}$  and  $V_{\text{pore}}$  values should be corrected. Eq. 1 can be rewritten as follows:

$$(V_{\text{solid}}^0 - \phi * V_{\text{solid}}^0) + (V_{\text{pore}}^0 + \phi * V_{\text{solid}}^0) = V_{\text{filter}} \quad (3)$$

If the filter is made up of several solids, their volumes ( $V_{\text{solid}}^{0,i}$ ), their proportions in the solid phase  $v_i$ , and their porosities ( $\phi_i$ ) should be considered. Eq. 3 is then rewritten to:

$$(V_{\text{solid}}^0 - \sum v_i * \phi_i * V_{\text{solid}}^{0,i}) + (V_{\text{pore}}^0 + \sum v_i * \phi_i * V_{\text{solid}}^{0,i}) = V_{\text{filter}} \quad (4)$$

Equation 4 is the general equation of filtration systems of granular particles. For  $\phi_i = 0$  (no porous material), the basic form (Eq. 1) is restored.

The application of Eq. 4 to the six systems of this study is summarized as follows:

$$\text{System 1: } V_{\text{sand}}^0 + V_{\text{pore}}^0 = V_{\text{filter}}$$

$$\text{System 2: } V_{\text{ZVI}}^0 + V_{\text{pore}}^0 = V_{\text{filter}}$$

$$\text{System 3: } V_{\text{PM}}^0 - \phi_{\text{PM}} * V_{\text{PM}}^0 + (V_{\text{pore}}^0 + \phi_{\text{PM}} * V_{\text{PM}}^0) = V_{\text{filter}}$$

$$\text{System 4: } (V_{\text{PIC}}^0 - \phi_{\text{PIC}} * V_{\text{PIC}}^0) + (V_{\text{pore}}^0 + \phi_{\text{PIC}} * V_{\text{PIC}}^0) = V_{\text{filter}}$$

$$\text{System 5: } v_{\text{sand}} * V_{\text{sand}}^0 + v_{\text{ZVI}} * V_{\text{ZVI}}^0 + V_{\text{pore}}^0 = V_{\text{filter}}$$

$$\text{System 6: } v_{\text{ZVI}} * V_{\text{ZVI}}^0 + v_{\text{PM}} * (V_{\text{PM}}^0 - \phi_{\text{PM}} * V_{\text{PM}}^0) + (V_{\text{pore}}^0 + v_{\text{PM}} * \phi_{\text{PM}} * V_{\text{PM}}^0) = V_{\text{filter}}$$

In the systems 5 and 6,  $v_{\text{ZVI}} = v_{\text{PM}} = v_{\text{sand}} (= 0.5)$  is added to account for the 1:1 dual mixture nature. The next important feature is the estimation of the initial volume of  $\text{Fe}^0$  ( $V_{\text{ZVI}}^0$ ) in individual systems. The application of Eq. 4 restricted to  $\text{Fe}^0$  yields:

$$\text{System 1 and 3: } V_{\text{ZVI}}^0 = 0$$

$$\text{System 2: } V_{\text{ZVI}}^0 = (1 - \Phi_0) * V_{\text{filter}}$$

$$\text{System 4: } V_{\text{ZVI}}^0 = (1 - \Phi_0) * V_{\text{filter}} - \phi_{\text{PIC}} * V_{\text{PIC}}^0$$

System 5 and 6:  $V_{\text{ZVI}}^0 = v_{\text{ZVI}} * (1 - \Phi_0) * V_{\text{filter}}$  ( $v_{\text{ZVI}} = 0.5$ )

The density of  $\text{Fe}^0$  ( $\rho_{\text{ZVI}}$ ) is supposed invariable in compact ZVI and porous PIC. The mass of  $\text{Fe}^0$  in each system is deduced from Eq. 5:

$$m_{\text{ZVI}} = \rho_{\text{ZVI}} * V_{\text{ZVI}}^0 \quad (5)$$

For the calculations of this study, the following numerical values are considered:  $V_{\text{filter}} = 1000 \text{ mL}$ ;  $\rho_{\text{ZVI}} = 7.8 \text{ g/cm}^3$ ;  $C = 0.64$ ;  $\Phi_0 = 0.36$ ;  $\phi_{\text{PIC}} = \phi_{\text{PM}} = 0.40$ . The critical porosity of sand [78] is arbitrarily considered for both porous media. The  $\rho_{\text{ZVI}}$  value ( $2.2 \text{ g/cm}^3$ ) of the sponge iron tested by Yi et al. [19] is inferior to the average density of sand ( $2.6 \text{ g/cm}^3$ ) and shows that a PIC porosity of 40 % is a realistic value. The porosity of PIC used in SONO filters (CIM) varies between 30 and 35 % [57].

### 3.2. Descriptive Aspects

The initial pore volume corresponding to a filter described above is  $V_{\text{pore}}^0 = \Phi * V_{\text{filter}} = 360 \text{ mL}$ . The corresponding volume of solid is  $V_{\text{solid}}^0 = 640 \text{ mL}$ . For porous materials like PIC and pumice, a fraction of  $V_{\text{solid}}^0$  is also a part of the total porosity. With a granular porosity of 40 % ( $\phi = 0.4$ ), the additional pore volume ( $V_p^0$ ) in systems containing porous materials is  $\phi * V_{\text{solid}}^0 = 256 \text{ mL}$ . In order words the systems with 100 % PIC or pumice result in an initial total pore volume of  $360 + 256 = 616 \text{ mL}$ . For dual 1:1 systems involving porous pumice ( $v_{\text{ZVI}} = v_{\text{PM}} = 0.5$ ), the  $V_p^0$  value is one half of 256 mL and the corresponding  $V_p^0$  value is 488 mL.

As concerning the solid fraction,  $V_{\text{solid}}$  is maximal in systems with compact materials ( $\text{Fe}^0$  and sand;  $V_{\text{solid}}^0 = 640 \text{ mL}$ ). The  $\text{Fe}^0$  fraction in the pure PIC system is  $V_{\text{solid}}^0 = (1 - \phi) * V_{\text{solid}}^0 = 384 \text{ mL}$ . In the dual  $\text{Fe}^0$  systems ( $\text{Fe}^0$ /pumice and  $\text{Fe}^0$ /sand),  $V_{\text{ZVI}}$  is one half of  $V_{\text{solid}}^0$  ( $V_{\text{ZVI}} = 320 \text{ mL}$ ).  $V_{\text{ZVI}}$  is essential to discuss the extent of  $\text{Fe}^0$  depletion and the corresponding porosity loss.  $V_{\text{ZVI}}$  can be occupied by 2.5 to 5.0 kg of  $\text{Fe}^0$  (density:  $7.8 \text{ g/cm}^3$ ) (Table 2).

The values in Table 2 confirm that the initial porosity is minimal (36.0 %) for systems containing compact particles ( $\text{Fe}^0$  and sand) and maximal (61.6 %) in systems containing porous particles (PIC and PM). In 1:1 mixing (vol/vol) a compact and a porous material, the initial porosity is 48.8 %. The next section will discuss the extent of  $\text{Fe}^0$  depletion as expansive iron corrosion is limited by the available pore volume.

**Table 2:** Evaluation of the initial  $\text{Fe}^0$  volume and the initial porosity in the five investigated systems. Calculations are made for a filter compactness of 64 % ( $C = 0.64$  or  $\Phi_0 = 0.36$ ) and a granular porosity of 40 % ( $\phi_0 = 0.40$ ) for the composite iron material (CIM) and pumice (PM).  $R^{\text{ox}}$  is the relative reactivity factor under oxic conditions.

System	$V^{\circ}_{\text{solid}}$ (mL)	$V^{\circ}_{\text{pore}}$ (mL)	$V^{\circ}_{\text{ZVI}}$ (mL)	$\Phi_0$ (%)	$m^{\circ}_{\text{ZVI}}$ (kg)	$V^{\circ}_{\text{ZVI}}$ (mL)	$P^{\text{anox}}_{\text{ZVI}}$ (%)	$P^{\text{ox}}_{\text{ZVI}}$ (%)	$R^{\text{ox}}$ (-)
Sand	640	360	0	36.0	0.00	0	-	-	-
ZVI	640	360	640	36.0	4.99	333.3	52.1	17.6	0.35
Pumice	384	616	0	61.6	0.00	0	-	-	-
CIM	384	616	384	61.6	3.00	570.4	100.0	50.1	1.00
ZVI/sand	640	360	320	36.0	2.50	333.3	100.0	35.2	0.70
ZVI/PM	512	488	320	48.8	2.50	541.9	100.0	47.7	0.95

### 3.3. $\text{Fe}^0$ Depletion and Porosity Loss

Section 3.2 has determined the mass of  $\text{Fe}^0$  contained in individual systems (Table 2). For the economy of the systems, it is essential to know the proportion at which the available  $\text{Fe}^0$  amount can be depleted. Iron corrosion is a volumetric expansive process. The volume of the corrosion product is higher than that of the original metal. The volumetric ratio ( $\eta$ ) between the expansive corrosion product ( $V_{\text{ox}}$ ) and the iron consumed ( $V_{\text{ZVI}}$ ) in the corrosion process is called “rust expansion coefficient” [73,74]. Basically, iron corrosion stops when there is no free space for expansive iron oxidation. That is when the excess volume ( $V_{\text{excess}} = V_{\text{ox}} - V_{\text{ZVI}}$ ) occupied by corrosion products is equal to the initial pore volume ( $V^{\circ}_{\text{pore}}$ ).

The excess volume contributing to filter clogging is given by  $V_{\text{excess}}$  in Eq. 6 [38,48,51].

$$(\eta - 1)V_{\text{ZVI}} = V_{\text{excess}} \quad (6)$$

Where,  $\eta$  ( $2.08 \leq \eta \leq 6.4$ ) is the coefficient of volumetric expansion [73].

The  $\text{Fe}^0$  filtration system is clogged when the volume  $V_{\text{excess}}$  is equal to the initial inter-granular voids ( $V^{\circ}_{\text{pore}}$ ). The corresponding  $\text{Fe}^0$  volume ( $V^{\circ}_{\text{ZVI}}$ ) is given by Eq. 7:

$$V^{\circ}_{\text{ZVI}} = \frac{V_{\text{excess}}}{(\eta - 1)} \quad (7)$$

The percentage of  $\text{Fe}^0$  depletion ( $P_{\text{ZVI}}$ , Table 2) is given by Eq. 8:

$$P_{\text{ZVI}} = \frac{V^{\circ}_{\text{ZVI}}}{V_{\text{excess}}} * 100 \quad (8)$$

$P_{\text{ZVI}} \geq 100$  % indicates that  $V^{\circ}_{\text{ZVI}} \leq V^{\circ}_{\text{pore}}$  and  $\text{Fe}^0$  depletion occurs before or just at complete clogging. Table 2 summarized the results of  $P_{\text{ZVI}}$  values for two different conditions: (i) anoxic conditions where  $\text{Fe}_3\text{O}_4$  ( $\eta = 2.08$ ) is the main corrosion product, and (ii) oxic conditions where  $\text{Fe}(\text{OH})_3$  ( $\eta = 4.2$ ) is the main corrosion product. For reference purpose, the coefficient of relative reactivity under oxic conditions ( $R^{\text{ox}}$ ) is also given. The PIC system served as the operational reference. Results indicate that under anoxic conditions, the pure  $\text{Fe}^0$  system is clogged when only 52 % of  $\text{Fe}^0$  is depleted. These results confirm the previous findings of Noubactep and colleagues [38,45-51], and reiterate that pure  $\text{Fe}^0$  filters are not sustainable under oxic conditions [55]. Accordingly, efforts should be directed at lowering dissolved  $\text{O}_2$  level on top of the  $\text{Fe}^0$  filter (e.g. using a biosand filter). Under oxic conditions, all systems will experience clogging before iron depletion. The increasing order of  $\text{Fe}^0$  depletion is:  $\text{Fe}^0 < \text{Fe}^0/\text{sand} < \text{Fe}^0/\text{PM} < \text{PIC}$ . These results (i) support the suitability of sand to sustain  $\text{Fe}^0$  filtration efficiency, (ii) corroborate the superiority of PM over sand in sustaining  $\text{Fe}^0$  filtration efficiency, and (iii) demonstrate the particular suitability of PIC for sustainable  $\text{Fe}^0$  filters.

Actually, various PICs have been presented (Table 1). The PIC (termed as CIM) presented by Hussam and colleagues [6,17,55-57] is clearly the most intensively tested (over the past 8 years). Several other non porous composites have been presented, including nano-scale multi-metallic systems [13,37,79,80]. In particular, Bojic and colleagues [81-84] developed an  $\text{Al}^0$ -based composite (micro-alloyed aluminium composite - MAIC) which was efficient to remove aqueous biological (e.g. *Escherichia coli*) and chemical (e.g.  $\text{Cr}^{VI}$ ,  $\text{Cu}^{II}$ , trihalomethanes) contamination.

Keeping in mind that  $\text{Al}^0$  is almost 'inert' under environmental conditions ( $P_{\text{CO}_2} = 0.035 \text{ %}$ ,  $T < 30 \text{ }^\circ\text{C}$ ), it seems that micro-alloying is the key to manufacture reactive materials with controllable reactivity. The need of materials with controllable reactivity is urgent because most of the available commercial materials are mixture of scrap material (e.g. Connelly, Peerless, Rheinfelden) whose final composition is even unknown from the 'manufacturers' [85-89].

## 4. DISCUSSION

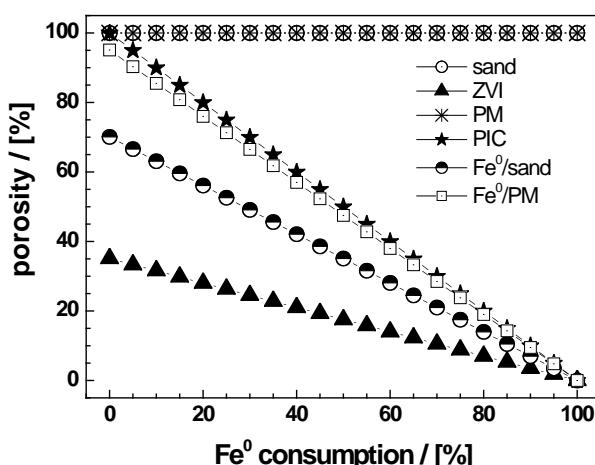
### 4.1. Lessons from SONO filters

The presentation, until now, has demonstrated the urgent necessity of using highly porous systems for sustainable  $\text{Fe}^0$ -based filtration systems. While highly inter-connected porous systems offer certainly sustained permeability, the efficiency for contaminant removal should be considered as well [15,32,54]. The calculations in Table 2 have rationalized the observed long term functionality (> 8 years) of efficient SONO arsenic filters containing a pure layer of porous CIM (5 to 10 kg making up a material layer of about 13 cm) [17]. Using the same design parameters with only 3 kg of iron chips (pure compact  $\text{Fe}^0$ ) lost its porosity within 6 months [6,55]. These results equally question the current rationale behind the functionality of subsurface  $\text{Fe}^0$  PRBs made up of 100 %  $\text{Fe}^0$  layers that have been working for more than 8 years [12]. A plausible explanation is the limited level of  $\text{O}_2$  in the subsurface. Another plausible explanation is the fact that used materials were not spherical and the initial porosity was larger than 36 % used in the calculations of this study [38,51]. For a traceable discussion, the intrinsic characteristics of the used materials, the initial subsurface conditions and their time-dependant variability should have been documented.

### 4.2. The Porosity of Tested Systems

The evolution of the porosity of the six systems [(a) to (f)], presented in Figure 1, is discussed in this section (Figure 2).

The first 3 systems (sand, ZVI and PM) are reference systems. The pure  $\text{Fe}^0$  system (ZVI) is a negative reference aiming at attesting that expansive iron corrosion causes system clogging in the short term ( $R^{\text{ox}}$  values, Table 2). System (a) and system (c) document the difference in using compact or porous materials. In both cases the particles are inert in water under environmental conditions. A porosity loss can

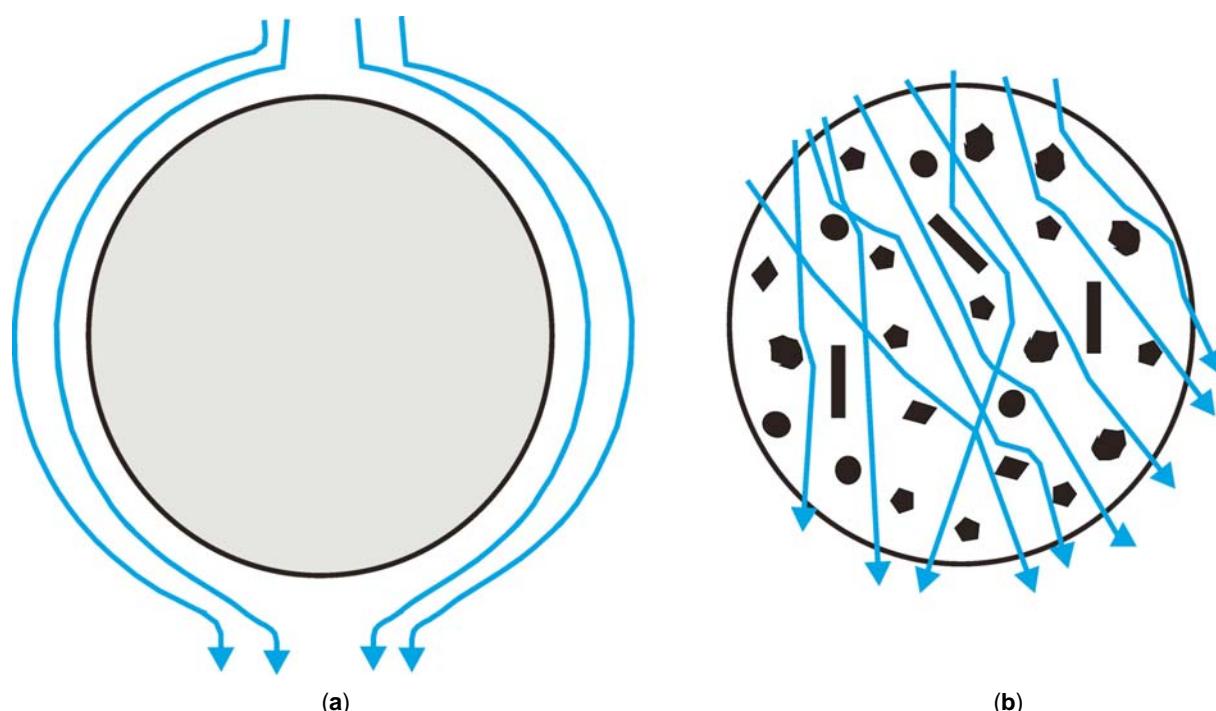


**Figure 2:** Comparison of the evolution of the relative porosity due to expansive iron corrosion under oxic conditions ( $\eta = 4.2$ ). The reference system (sand or pumice) experiences no porosity loss. For the  $\text{Fe}^0$ -based systems, the relative porosity is normalized by the extend of  $\text{Fe}^0$  depletion ( $P_{\text{ZVI}}$ ) using the PIC system as reference. The suitability of porous materials (e.g. PIC, PM) for sustainable permeable systems is corroborated.

only result from accumulation or precipitation of inflowing species and/or contaminants within the (interconnected) pores. The discussion of porosity loss due to the accumulation of foreign precipitates is out of the scope of this study. Such systems have been used in water and wastewater treatment for decades [90-100].

The remaining systems [(d), (e) and (f)] are reactive systems in which  $\text{Fe}^0$  sustainability (long term efficiency) is supported by (i) using granular porous CIM, or (ii) admixing granular compact  $\text{Fe}^0$  to inert species (compact sand and porous pumice). As discussed above, system (d) (pure PIC) is the most sustainable system in terms of delay in porosity loss. It is essential to notice that the space occupied by sand in system (e) ( $\text{Fe}^0/\text{sand}$ ) is totally lost as it neither contributes to water flow nor stores fouling agents (iron corrosion products) (Figure 3). The intra-particle pore space in system (f) ( $\text{Fe}^0/\text{PM}$ ) may be accessible to store iron corrosion products. However, quantitative transport of dissolved and colloidal iron species into the porous structure of pumice can not be guaranteed, even in case they are really interconnected. Therefore, the extent of occupation of the pores of pumice by iron corrosion products is difficult to assess.

Another important feature favoring the application of porous PIC is that the internal surface of the grains is in contact with water and do corrode [10,59,60]. This phenomenon has two advantages: (i) contaminant removal by size-exclusion occurs also within the intra-



**Figure 3:** Schematic layout of water flow: (a) around a compact particle and (b) through a porous particle. The space occupied by a compact particle is 'lost' whereas the intra-granular porosity of porous particles can be exploited as space for expansive iron corrosion.

granular porosity and (ii) the probability of porous  $\text{Fe}^0$  ( $\phi = 0.4$ ) depletion increases as the corrosion kinetics are increased comparatively to the case of a compact  $\text{Fe}^0$  material ( $\phi = 0$ ). For this reason, it is likely that the order of sustainability obtained here by comparing the extent of porosity loss (Figure 2) is replicated in contaminant removal experiments. However, the evolution of individual systems will depend on two fundamental parameters: (i) intrinsic reactivity of  $\text{Fe}^0$  materials, and (ii) the water flow velocity. Hence, the objective of this article is to motivate the manufacture of various porous composites for site-specific applications.

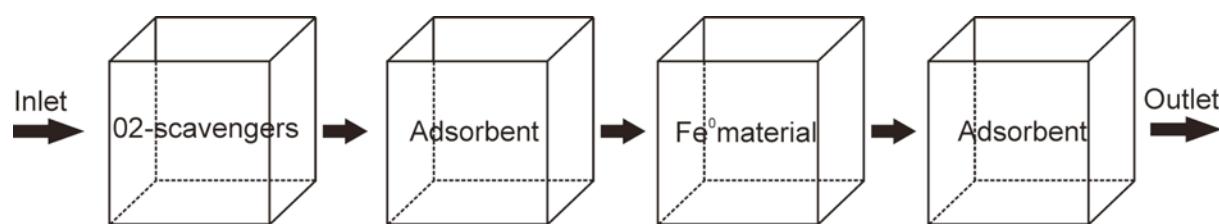
While existing approaches mostly collectively earn for more reactive materials (including nano-scale composites) [37,80], the present study advocates for manufacturing appropriate (porous) materials for site-specific applications. To the best of the author's knowledge, only Li *et al.* [101] have intentionally alloyed  $\text{Fe}^0$  to decrease its reactivity. However the objective of the authors [101] was to reduce the iron level in the filter effluent. As experimentally demonstrated by several authors [15,30,32,33] this increased iron level is the expression of initial increased reactivity. The iron level was lowered to values less than 1 mg/L within some 6 weeks. In other words, properly micro-alloying  $\text{Fe}^0$  alone will not solve

the clogging problem. Therefore, reactive porous iron composites are urgently needed.

#### 4.3. Designing the Next Generation $\text{Fe}^0$ Filter

Metallic iron is the reactive material in  $\text{Fe}^0$ -based filters.  $\text{Fe}^0$  oxidizes to produce iron hydroxides and oxides for the elimination of biological and chemical contamination by adsorption, co-precipitation and size-exclusion [79,102-107]. The process of progressive transformation of  $\text{Fe}^0$  to iron oxides is well-described in the literature and will not be repeated here [8,108-112]. It is just to recall that strictly compact  $\text{Fe}^0$  is transformed through several steps of porous iron hydroxides (e.g.  $\text{Fe(OH)}_2$ ,  $\text{Fe(OH)}_3$ ) to almost compact oxides (e.g.  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeOOH}$ ) [34-36]. During this dynamic process nascent iron hydroxides adsorb and co-precipitate contaminants while less reactive oxides just adsorb dissolved species. All types of iron species (reactive and less reactive) contribute to contaminant removal by size-exclusive filtration as their formation occupies the inter-particular voids [34].

The present study has demonstrated the crucial importance of developing more efficient  $\text{Fe}^0$  materials: porous iron composites. Once a new  $\text{Fe}^0$  material is developed (e.g. micro-alloyed PIC), four scientific aspects need to be understood: (i) the long-term behaviour of iron corrosion (corrosion kinetics at



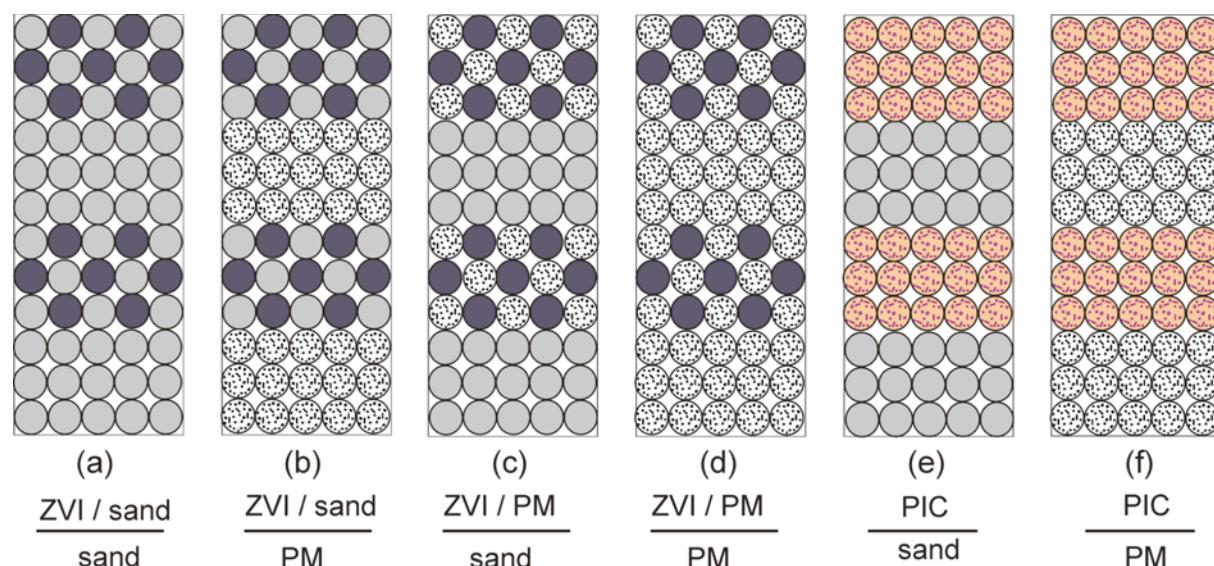
**Figure 4:** Concept of treatment train combining contaminant removal in  $\text{Fe}^0/\text{H}_2\text{O}$  systems and successive systems containing adsorbents. The primary aim of the O<sub>2</sub>-scavenger is to create anoxic conditions for sustainable  $\text{Fe}^0$  filtration.

pseudo-equilibrium), (ii) the kinetics of contaminant removal at pseudo-equilibrium of iron corrosion, (iii) the water flow velocity compatible with satisfactorily water treatment, and (iv) the time-dependant evolution of the filter permeability as impacted by expansive iron corrosion. The profound knowledge of these four key aspects determines the mass of  $\text{Fe}^0$  needed to manufacture a filter with a specific capacity for a certain group of contaminants. The contaminant affinity to iron oxides significantly determines the filter design [32,33,77]. Contaminants with low affinities to iron corrosion products must be removed before the  $\text{Fe}^0$  filter. The in-depth knowledge of the nature and the extent of contamination determine the physical designs of a treatment system. These design efforts could be supported by modern numerical modelling algorithms and tools, including finite element methods for the solution of mass-transport equations [57].

$\text{Fe}^0$ -based filters have been suggested as a stand-alone technology for the treatment of waters with unknown chemical and microbial quality [8,23,34,36]. Therefore, beside  $\text{Fe}^0$ , water filters require active adsorbents to accumulate species with low affinity to

iron oxides (e.g. cationic dyes) and species exceeding the  $\text{Fe}^0$  unit. Relevant adsorbents include sand, activated carbon, and wood charcoal. The presentation above suggests that for a sustainable  $\text{Fe}^0$  unit, the level of dissolved O<sub>2</sub> should be considerably reduced. Therefore, a biosand filter or any other O<sub>2</sub>-scavenging unit is necessary on top of the  $\text{Fe}^0$ -unit. Figure 4 depicts the general sequence of efficient  $\text{Fe}^0$ -based water treatment plants.

The  $\text{Fe}^0$ -unit, which is the heart of the filtration system can advantageously contain several inert granular materials including anthracite, blast furnace slag, brick chips, crushed stones, gravel, pumice or sand to impart mechanical stability and regulate the hydraulic conductivity. The role of these species in sustaining iron corrosion has already been discussed above, such as sand and pumice as admixing agent or dispersant in  $\text{Fe}^0/\text{PM}$  and  $\text{Fe}^0/\text{sand}$  systems. Figure 5 presents some schematic representations of possible configurations of the  $\text{Fe}^0$  unit. It is expected that by varying the granulometry and the thickness of the inert material layer (PM or sand), various levels/scales of the hydraulic conductivities can be achieved. Another



**Figure 5:** Schematic layout of six possible embodiments of  $\text{Fe}^0$ -based materials for sustainable filtration systems. Depending on the site of the treatment systems individual layers could be contained in separated beds.

possible advantage of sandwiching pumice layer between reactive zones is the accumulation of iron corrosion. So that short-distance transport of iron (hydr)oxides is more likely to occur than in thicker beds. It must be noted that SONO filters was developed on the basic idea of using  $\text{Fe}^0$  as generator of soluble Fe species to favour As removal in sand filters [113-116].

## 5. CONCLUDING REMARKS

There are some evidences that porous composites improve the performance of  $\text{Fe}^0$ -based filtration systems. The extent of material exhaustion is optimal in these systems as well. Whilst the demonstrated principle of the fundamental suitability of porous composites has a universal validity, target experiments with well characterized (new) materials are needed to understand more precisely the clogging phenomenon in granular  $\text{Fe}^0$ -based filters. Relevant experiments will assess the influence of (i) composite type (intrinsic reactivity), (ii) composite porosity, (iii) composite particle size, (iv) general filter design (depth of filter, layering arrangement with particles of different sizes, compaction of the media during construction), (v) chemistry of inflowing water (nature and concentration of dissolved species, turbidity) and (v) the frequency of filtration events (intermittent filters).

The overall results of these investigations will improve the understanding of the efficiency of  $\text{Fe}^0$  filters as impacted by the clogging phenomenon. The ultimate aim is to build a sound basis for a system-independent design of  $\text{Fe}^0$  filters. Once a reliable design guidance is available, predicting site-specific filter's hydraulic and treatment performances along with their lifespan could be fine-tuned by pilot studies. One of the main applications of such a tool would be an improved design of above-ground water treatment systems for decentralized safe drinking water provision (Figure 4).

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## ABBRIAVATION

CIG = composite iron granules

CIM = composite iron matrix

DRI	= direct reduced iron
MAIC	= micro-alloyed aluminium composite
PIC	= porous iron composite
PM	= pumice
PRB	= permeable reactive barriers
SMI	= sulfur-modified iron
ZVI	= zero-valent iron

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