Effect of pumice and sand on the sustainability of granular iron beds for the aqueous removal of Cu$^{II}$, Ni$^{II}$, and Zn$^{II}$

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Running Title: Admixing pumice and sand to reactive Fe$^0$ sustains long-term metal removal.

Acronym List

PRB Permeable Reactive Barrier

Keywords: Hydraulic conductivity, Reactive barriers, Pumice, Sand, Zerovalent iron.
Abstract

Current knowledge of the basic principles underlying the design of Fe$^0$ beds is weak. The volumetric expansive nature of iron corrosion was identified as the major factor determining the sustainability of Fe$^0$ beds. This work attempts to systematically verify developed concepts. Pumice and sand were admixed to 200 g of Fe$^0$ in column studies (50:50 volumetric proportion). Reference systems containing 100 % of each material have been also investigated. The mean grain size of the used materials (in mm) were 0.28 (sand), 0.30 (pumice) and 0.50 (Fe$^0$). The five studied systems were characterized (i) by the time dependent evolution of their hydraulic conductivity (permeability) and (ii) for their efficiency for aqueous removal of Cu$^{II}$, Ni$^{II}$, and Zn$^{II}$ (about 0.30 M of each). Results showed unequivocally that (i) quantitative contaminant removal was coupled to the presence of Fe$^0$, (ii) additive admixture lengthened the service life of Fe$^0$ beds, and (iii) pumice was the best admixing agent for sustaining permeability while the Fe$^0$/sand column was the most efficient for contaminant removal. The evolution of the permeability was well-fitted by the approach that the inflowing solution contained dissolved O$_2$. The achieved results are regarded as starting point for a systematic research to optimise/support Fe$^0$ filter design.

1 Introduction

Permeable reactive barriers (PRBs) containing metallic iron (Fe$^0$) as reactive medium have been developed during the past two decades to an established technology for groundwater remediation [1-11]. The original PRB technology containing granular Fe$^0$ has been expanded to the injection of nano-scale Fe$^0$ for source remediation [8-11]. To date, more than 180 Fe$^0$ PRBs have been installed worldwide [8,11]. Successful accomplishment of remedial goals has been typically reported. At some few sites, system failures were recorded [8,12]. Reported failures were attributed to design shortcomings due to poor site characterization (reason 1), poor design selection (reason 2) or installation at sites where the technology is not an appropriate choice (reason 3) [8,12,13]. However, there is clear evidence that the physico-chemistry of the Fe$^0$/H$_2$O system was not properly
considered [14]. Accordingly, design shortcomings may have reasons different from or additional to reasons 1, 2 and 3.

A major concern of Fe\textsuperscript{0} PRBs is related to the reduction of the hydraulic conductivity (permeability loss) with time [15-17]. Laboratory and field data have also demonstrated diminished Fe\textsuperscript{0} reactivity with time [9, 18]. Consequently, the sustainability of Fe\textsuperscript{0} PRBs in terms of both Fe\textsuperscript{0} reactivity and system permeability has been extensively discussed during the past 15 years [1,18-24]. Reported results are confusing and even conflicting as demonstrated below for trichloroethene (TCE).

O’Hannesin and Gillham [1] reported on successful TCE (268 mg/L) reductive degradation by a Fe\textsuperscript{0}/sand mixture containing 22 % Fe\textsuperscript{0} by weight (laboratory and field test). Bi et al. [21] tested several weight Fe\textsuperscript{0}/sand mixtures (25/75, 50/50, 75/25, 85/15 and 100/0) for TCE (up to 60 mg/L) treatment and reported that the system with less than 50 % Fe\textsuperscript{0} was not efficient (laboratory test). Ruhl et al. [18] evaluated four dual mixtures (Fe\textsuperscript{0}/anthracite, Fe\textsuperscript{0}/gravel, Fe\textsuperscript{0}/pumice and Fe\textsuperscript{0}/sand) for TCE (about 10 mg/L) treatment (laboratory test). The used masses of additives varied from 24.4 g for pumice to 104.3 g for gravel. The used mass of Fe\textsuperscript{0} was 100 g resulting in Fe\textsuperscript{0} weight ratios varying from 49 % for gravel to 80 % for pumice. Ruhl et al. [18] concluded that tested dual systems are not applicable for TCE treatment but “might be applicable for the removal of heavy metals”.

The three examples reveal that researchers use varying experimental procedures to characterize processes in Fe\textsuperscript{0}/H\textsubscript{2}O systems (see Tab. 1) [1,21,25-33]. These procedures differ for instance in Fe\textsuperscript{0} intrinsic reactivity, Fe\textsuperscript{0} pre-treatment, Fe\textsuperscript{0} mass, Fe\textsuperscript{0} particle size and shape, used admixing additives and their proportions, duration of the experiments, nature and concentration of the contaminant, buffer application, solution flow velocity and water chemistry. As a result, many different reports for the same compound are available in the literature (even for the same Fe\textsuperscript{0}).

Water and dissolved inorganic constituents (Ca\textsuperscript{2+}, HCO\textsubscript{3}\textsuperscript{-}, Mg\textsuperscript{2+}, O\textsubscript{2}, PO\textsubscript{4}\textsuperscript{3-}, SO\textsubscript{4}\textsuperscript{2-}) react with iron species (Fe\textsuperscript{0}, Fe\textsuperscript{II} and Fe\textsuperscript{III}) to form precipitates that progressively fill the inter-particular porosity
within a $\text{Fe}^0$ filter. The potential of these in situ generated precipitates to limit the permeability and the efficiency of $\text{Fe}^0$ PRBs filters has been clearly documented [1,4,6-8]. However, the role of $\text{Fe}^0$ oxidation by water has not always been properly considered and the role of gas ($\text{H}_2$) formation in porosity/permeability loss has been sometimes overestimated [15,16]. Recent theoretical works demonstrated that a $\text{Fe}^0$-based filter should be considered as a system in which iron is corroded mostly by water and the micro-pollutants are sequestered in the matrix of precipitation corrosion products [14,34-36]. This view corroborates concordant reports regarding $\text{Fe}^0$ filters as a long-term sink for C, S, Ca, Si, Mg, and N [12,37-39].

The present work is an attempt to improve the design of $\text{Fe}^0$ filtration systems based on recent theoretical studies [14]. In the present work, the efficiency of five different systems (A to E) for aqueous contaminant removal is tested in column studies. The volumetric composition of individual systems is given as: (A) 100 % sand, (B) 100 % pumice, (C) 100 % $\text{Fe}^0$, (D) 50:50 $\text{Fe}^0$:pumice, and (E) 50:50 $\text{Fe}^0$:sand. The model solution contained about 0.30 M of Cu$^{\text{II}}$, Ni$^{\text{II}}$, and Zn$^{\text{II}}$. The evolution of the systems is characterized by determining the (i) extent of contaminant removal, and (ii) evolution of hydraulic conductivity.

2 Materials and methods

2.1 Chemicals and solutions

Copper(II) nitrate hydrate (purity 99.999), nickel(II) nitrate hexahydrate (purity 99.999) and zinc(II) nitrate hexahydrate (purity 99.000) were obtained from Sigma-Aldrich. All chemicals used for experiments and analysis were of analytical grade. The used solutions were obtained by dissolving copper nitrate, nickel nitrate and zinc nitrate in distilled water. The molar concentration of the resulting solution was as follows: 0.27 M Cu, 0.29 M Ni and 0.37 M Zn. The corresponding mass concentrations are 17 mg/L Cu, 17 mg/L Ni, and 23 mg/L Zn.

2.2 Solid materials

2.2.1 Porosity of binary granular media
The total porosity $\Phi$ of a binary granular medium composed of two kinds of particles $P_1$ and $P_2$ (here $P_1$ corresponds to $Fe^0$ particles) is given by:

$$\Phi = \Phi_{\text{inter}} + \Phi_{\text{pp}}, f_{\text{pp}} = \left[1 - \frac{V_{a1} + V_{a2}}{V_{rz}}\right] + \phi_2 \cdot \frac{V_{a2}}{V_{rz}}$$

$$\Phi = \left[1 - \frac{M_1 / \rho_{a1} + M_2 / \rho_{a2}}{V_{rz}}\right] + \phi_2 \cdot \frac{M_2 / \rho_{a2}}{V_{rz}}$$

(1)

Where: (i) $\Phi_{\text{inter}}$ is inter-particular porosity (ii) $V_{a1}, M_{a1}, \rho_{a1}$ are respectively the apparent volume of the particles $i$, the mass and the apparent specific weight, and $\phi_2$ is the intra-particular porosity of the particles 2 with $\phi_2 = 0$ for non porous particles (sand) and $\phi_2 \neq 0$ for porous particles (pumice) and (iii) $V_{rz}$ is the total packing volume of the granular medium.

### 2.2.2 Metallic iron ($Fe^0$)

The used $Fe^0$ is of the type FERBLAST RI 850/3.5, distributed by Pometon S.p.A., Mestre - Italy.

The powdered material contents mainly iron (> 99.74 %). Identified impurities included mainly Mn (0.26 %), O, S and C. The material is characterized by uniform grain size distribution. The coefficient of uniformity $U$ (ratio between the diameters corresponding to 60 and 10 % finer in the grain size distribution) is 2. The mean grain size ($d_{50}$) is about 0.5 mm and the initial porosity of used $Fe^0$ medium has been estimated to be $\Phi_0 = 49.6$ % (see Tab. 2, Eq. 1).

### 2.2.3 Pumice

The used pumice originates from Lipari (Aeolian Islands, Sicily – Italy). Its mineralogical composition was determined as follows: $SiO_2$: 71.75 %; $Al_2O_3$: 12.33 %; $K_2O$: 4.47 %; $Na_2O$: 3.59 %; $Fe_2O_3$: 1.98 %; moreover it contains about 4 % of bound water entrapped in the pumice structure during the sudden cooling of magma and traces of other compounds (e.g. $CaO$, $SO_3$, $MgO$, $TiO_2$, $FeO$, $MnO$, $P_2O_5$). The material is characterized by uniform grain size distribution. The coefficient of uniformity $U$ is 1.4. The mean grain size ($d_{50}$) is about 0.3 mm. This type of pumice has been chosen since it was the available fraction closest to $Fe^0$ in dimension. The initial porosity of the
pumice granular medium has been estimated to be $\Phi_0 = 73.3\%$ and the inner porosity of the pumice (intra particular porosity $\varphi_{pp}$) to be 41% (Tab. 2, Eq. 1) through Mercury Intrusion Porosity (MIP) measurements under the hypothesis that the relative density (packing) of granular mixtures in the columns and during MIP experiments were the same.

### 2.2.4 Sand

The used quartz sand was obtained from a river quarry. The sand was carefully washed with distilled water and sieved before use. The material is characterized by uniform grain size distribution. The coefficient of uniformity $U$ is 2.2. The mean grain size ($d_{50}$) is about 0.28 mm. The material was used without any further characterization. The initial porosity of the sand medium has been estimated to be $\Phi_0 = 45.0\%$ (Tab. 2, Eq. 1).

### 2.3 Column operation

Laboratory scale polymethyl methacrylate (Plexiglas) columns were operated in up-flow mode. The influent solution was pumped upwards from a single PE bottle using a precision peristaltic pump (Ismatec, ISM930). The flow rate was maintained constant at a value of 0.5 mL/min. Tygon tubes were used to connect inlet reservoir, pump, columns and outlet. Five plexiglas columns (50 cm long, 5.0 cm inner diameter) were used in the experiments (Fig. 1).

Five different systems were investigated (Systems A through E) (Tab. 3). System A was the operational reference system containing only sand (0 % Fe$^0$), System B was the second operational reference containing only pumice (0 % Fe$^0$) and system C was a pure iron bed (100 % Fe$^0$). The volumetric proportion of Fe$^0$ in the 2 other systems (D, E) was 50 %. In systems C to E, the mass of iron was fixed to 200 g. This mass represented either 100 % of the reactive zone (rz) or the relevant volumetric proportion of rz (Fig. 1, Tab. 3). In system B the pumice volume was set to be the same occupied by Fe$^0$ in system C while the pumice mass was obviously the same as in system E. The total porosity of the all systems varies between 45 % and 73 % (Tab. 2, Eq. 1).
The hydraulic conductivity [40] was determined during the column tests, by either constant-head (k > 10^{-6} m/s) or variable-head (k < 10^{-6} m/s) permeability methods, at selected dates to assess the permeability of the systems. The experiments were performed at room temperature (21 ± 4 °C). Samples for analysis were collected at periodic intervals and the experiments where prolonged until contaminant breakthrough (systems A and B) or a significant loss of the hydraulic conductivity (systems C to E) was observed.

2.4 Analytical methods

Samples from the columns were centrifuged at 3000 rpm (ALC, PK121 Multispeed Centrifuge). The supernatant was vacuum filtered through a 0.45 μm glass filters. The aqueous concentrations of Cu, Fe, Ni and Zn were then measured by Atomic Absorption Spectrophotometry (AAS - Shimadzu AA – 6701F; wavelengths: Cu 324.75 nm, Ni 232.00 nm, Zn 213.86 nm, Fe 248.33 nm) using air-acetylene flame and according to conventional Standard Methods [41]. The used AAS device was calibrated using three operational standard solutions covering the expected concentration range of the samples (after dilution if applicable). Each operational standard solution was prepared by an appropriate dilution of a 1000 ppm (Cu(NO₃)₂, Fe(NO₃)₃, Ni(NO₃)₂, Zn(NO₃)₂) certified atomic absorption stock solution from Merck (Germany). The minimum correlation coefficient of calibration curves was of 0.997. The pH value was measured by combination glass electrodes (WTW GmbH, inolab pH/Cond 720).

2.4.1 MIP measurements

MIP measurements have been carried out using a Micromeritics instrument apparatus type (AutoPore IV 9500). The instrument is capable of a minimum intruding pressure of 3.4 kPa and a maximum pressure of 227 MPa, so that the pore radius ranges from 2.7 nm to 180 μm.

For pumice particles the measured pore data allow determining the inter-particular and intra-particular porosities of the pumice particles, the apparent specific weight ρ_{ap} (defined as the ratio of the mass and the apparent volume of the pumice particles) and the specific weight ρ_s (defined as the
ratio of the mass and the volume of the solid phase of the pumice particles).

2.5 Expression of the experimental results

In order to characterize the magnitude of tested systems for contaminant removal, the removal efficiency (E) and the specific removal (E_s) were calculated using Eq. 2 and Eq. 3 [33].

\[ E = \frac{m_{\text{rem}}}{m_{\text{in}}} \times 100 \]  \hspace{1cm} (2)

\[ E_s = \frac{m_{\text{rem}}}{m_{\text{Fe}}} \times 100 \]  \hspace{1cm} (3)

where \( m_{\text{in}} \) is the mass of contaminant flowed into the column, \( m_{\text{rem}} \) is the mass of removed contaminant, and \( m_{\text{Fe}} \) the mass of Fe^0 present in the column.

2.6 Evaluation of the residual porosity

When iron corrodes, porous oxide layers are formed at the Fe^0/H_2O interface. The volume of the corrosion product (\( V_{\text{oxide}} \)) is higher than that of the original metal (\( V_{\text{Fe}} \)). The ratio (\( \eta \)) between the volume of expansive corrosion product and the volume of iron consumed in the corrosion process is called “coefficient of volumetric expansion” [42,43]. Generally, \( V_{\text{oxide}} \) is 2.08 to 6.40 times larger than \( V_0 \) (2.08 ≤ \( \eta \) ≤ 6.40 for free expansion).

At any time (\( t > 0 \)), \( V_{\text{oxide}} \) can be calculated using Eq. 4:

\[ V_{\text{oxide}} = \eta \times (V_0 - V_t) \]  \hspace{1cm} (4)

Where \( \eta \) is the coefficient of volumetric expansion, \( (V_0 - V_t) \) is the consumed Fe^0 volume with \( V_0 \) the initial volume of Fe^0 and \( V_t \) its residual Fe^0 at time \( t \).

The effective volumetric expansion \( \Delta V \) (Eq. 5) corresponding to the volume of pores that is occupied by iron corrosion products is a measure of the extent of porosity loss.

\[ \Delta V = (\eta - 1) \times (V_0 - V_t) \]  \hspace{1cm} (5)

The residual porosity of the system at time \( t \) (\( \Phi(t) \)) may be estimated by (Eq. 6):

\[ \Phi(t) = \Phi_0 - \frac{(\eta - 1) \times (V_0 - V_t)}{V_{\text{rz}}} \]  \hspace{1cm} (6)

Where \( \Phi_0 \) is the initial porosity of the reactive zone given in Tab. 3, and \( V_{\text{rz}} \) is the volume of the
3 Results and discussion

3.1 pH variation and Fe breakthrough

Metal ions are known to be removed from the aqueous phase in packed Fe\textsuperscript{0} beds by adsorption, coprecipitation and adsorptive size-exclusion when the pH > 4.5 [44-48]. Figure 2a clearly demonstrates that the pH value of the initial solution (t = 0) and that of the effluent from all columns was larger than 5.5. This suggests that contaminant removal could be quantitative (see Tab. 4) if the residence time is sufficient to enable the formation of enough iron corrosion products for contaminant retention in the column. A hint that quantitative contaminant removal was likely is given by the evolution of the iron concentration (Fig. 2b). Fig. 2b clearly shows that the effluent iron concentration was less than 0.2 mg/L and reached values close to up to 1 mg/L only shortly before clogging for the system with 50 % pumice (system E). This observation could be attributed to accelerated transport through preferential flow paths [26].

3.2 Metal breakthrough

Fig. 3 and Tab. 4 summarize the results of contaminant removal in systems containing Fe\textsuperscript{0}. It is clear from Fig. 3a that no Cu breakthrough occurs. Ni breakthrough occurs first (Fig. 3b). In fact Ni breakthrough occurs before day 8 in the system with 100 % Fe\textsuperscript{0}. Zn is the next less retained metal with a breakthrough occurring at day 10 in the system with 100 % Fe\textsuperscript{0} (Fig. 3c). The observed order of removal efficiency corresponds to the selectivity sequence for iron oxides and soils: Ni < Zn < Cu [49-51]. For example, Fontes and Gomes [50] found that in competitive adsorption Cu\textsuperscript{II} maintains its strong affinity with the surface, while Ni\textsuperscript{II} and Zn\textsuperscript{II} are displaced from the surface. This observation corroborates the view that species with higher affinity to iron oxides are better treated by Fe\textsuperscript{0} filters [23,24,52,53].

Another important result from Fig. 3 is that no contaminant breakthrough was observed in the system with 50 % sand (system D). This system is less porous than the system with 50 % pumice
(Tab. 3). The differential behaviour of the systems with pumice and sand (D and E) illustrates the dilemma of sustaining efficiency (maximum Fe\(^0\) ratio) while maintaining permeability, for instance by using porous pumice in place of sand [33]. As discussed in details elsewhere [14,36] this dilemma could be solved by using an appropriate thickness of the Fe\(^0\)-based layer for each relevant additive (e.g. activated carbon, anthracite, gravel, pumice, sand) to achieve water treatment under site specific conditions. Relevant site specific parameters include the nature of contaminant, the water chemistry and the water flow velocity. In other words, a proper design (reason 2, § 1) should be extended to the width of the Fe\(^0\) PRB, the nature of the admixing agent (e.g. type and grain size distribution) and the proportion of Fe\(^0\) therein.

The last important issue on contaminant breakthrough concerns the suitability of specific removal (Eq. 3) for a dynamic system in which reactive species are progressively generated. \(E_s\) values from Tab. 4 show that the lowest specific removal (1.74 mg Ni/g Fe\(^0\)) was obtained in system C (100 % Fe\(^0\)). While this result seems contradictory, it corroborates the view that iron corrosion is self-inhibitory and that decreasing the proportion of Fe\(^0\) is a powerful tool to increase sustainability ([54] and ref. cited therein). Tab. 5 shows that correcting \(E_s\) by considering the extent of Fe\(^0\) depletion at \(t_{\text{limit}}\) \((E_{s,\text{eff}})\) restores the intuitive trend that “the greater the adsorbent amount, the larger the \(E_s\) value”. Accordingly, the highest \(E_{s,\text{eff}}\) values were obtained in system C (absolute value) which clogged at first. This result corroborates previous findings that filtration systems containing a 100 % Fe\(^0\) layer are efficient but not sustainable [55,56]. Moreover, the fact that the effective specific removals for the three systems are similar \((4.0 \leq E_{s,\text{eff}} \leq 6.8)\) is a hint that the calculation of the consumed iron is right. Note that, \(E_{s,\text{eff}}\) values are derived from \(E_s\) values on the basis of the extent of Fe\(^0\) depletion at \(t_{\text{limit}}\) \((E_s, t_{\text{limit}})\), not at the depletion at the end of the experiment. This result means that no significant breakthrough was observed before \(t_{\text{limit}}\).

3.3 Hydraulic conductivity
The results presented in Fig. 4 clearly demonstrate that the hydraulic conductivity decreases with time for the systems containing Fe\(^0\) particles (systems C, D, E) then remains constant at time \(t_{\text{limit}}\) (Tab. 5).

The initial hydraulic conductivity \(K_0\) for all systems is about \(5.10^{-4}\) m/s. The hydraulic conductivity tends to about the limit value \(K_{\text{limit}} = 5.10^{-9}\) m/s at time \(t_{\text{limit}}\). The results show that the decrease of the permeability is down to about five orders of magnitude \(K_0/K_{\text{limit}} = 1.10^{-5}\). The time \(t_{\text{limit}}\) seems to depend on the investigated system (Tab. 5). The data in Tab. 5 clearly indicate that Fe\(^0\) admixture with sand and pumice resulted in extended service life. The longest service life was observed for the system with pumice particles and is consistent with the fact that intra-particle porosity has contributed to increased permeability [57,58].

Among the proposed models in the literature, the Kozeny-Carman equation is often considered to evaluate the evolution of the hydraulic conductivity [59]. This equation was developed after considering a porous material as an assembly of capillary tubes and yielded the hydraulic conductivity \(K\) as function of the porosity \(\Phi\), the specific surface \(S\) (m\(^2\)/kg of solids) and a factor \(C\) to take into account the shape and tortuosity of channels. The first approximation is to accept the Kozeny-Carman equation [60-64]:

\[
K(t) = K_0\left(\frac{\Phi}{\Phi_0}\right)^3 \left(\frac{1-\Phi_0}{1-\Phi}\right)^2
\]  

where \(K_0\) is the initial hydraulic conductivity and \(\Phi_0\) the initial porosity.

For the evaluation of the residual porosity \(\Phi\) as a function of the time \(t\), uniform corrosion for spherical particles with initial radius \(R_0\) (here \(R_0 = 500\) \(\mu\)m) is assumed. Individual particles corrode independently with the same kinetics until material depletion. Under these assumptions, it is considered that the actual radius \(R(t)\) of Fe\(^0\) particles varies linearly with time \(t\) according to:

\[
R(t) = R_0 - \frac{R_{0,t}}{t_{\text{depletion}}}
\]  

where \(R_{0,t}\) is the initial radius of the particles and \(t_{\text{depletion}}\) is the time of material depletion.
where \( t_{\text{Fe, depletion}} \) is the time at \( \text{Fe}^0 \) depletion.

From Eq. 5, 6 and 7, it is possible to simulate the decrease of the hydraulic conductivity as a function of time (Figure 4b-d). The modelling has been applied for the coefficient of volumetric expansion \( \eta = 6.40 \) in coherence with high \( \text{O}_2 \) levels and for two times at \( \text{Fe}^0 \) depletion (\( t_{\text{Fe, depletion}} = 50 \text{ days} \) and \( 62.5 \text{ days} \)) [43]. It can be noticed that the maximum volume of \( \text{Fe}^0 \) which may corrode is the one which leads to clogging \( (V_{\text{Fe, clogging}}) \) and is expressed by:

\[
V_{\text{Fe, clogging}} = \frac{\Phi_0 \cdot V_{rz}}{\eta - 1}, \quad (8)
\]

At time \( t_{\text{limit}} \) it is assumed that the volume of consumed \( \text{Fe}^0 \) tends to the one leading to the clogging of the column \( (V_t = 1.01 \cdot (V_0 - V_{\text{Fe, clogging}})) \) in calculations) and remains constant for \( t > t_{\text{limit}} \). Under these assumptions, the permeability \( K_{\text{limit}} \) corresponding to the time \( t_{\text{limit}} \) is reached at the clogging of the columns \( (\Phi \approx 0, \text{see Tab. 5}) \). The obtained results show that there is a good agreement between experiment and modelling concerning the kinetic of the decrease of the permeability with time and the \( K_{\text{limit}} \) value. It can be noticed that the linear law for corrosion process (Eq. 7) with the two considered times \( (t_{\text{Fe, depletion}}) \) as a first approximation of corrosion kinetic, allows to well reproduce the decrease of the permeability at the beginning of the filtration process. However, the evolution of the permeability around \( t_{\text{limit}} \) can not be accurately predicted.

The proposed modelling is a first attempt to predict the time-dependent decrease of the hydraulic conductivity (permeability loss) on the basis of the volumetric expansion of corroding iron. This work shows that the evolution of the hydraulic conductivity may be predicted without considering the evolution of the tortuosity or the specific surface in the Kozeny-Carman equation and is the consequence of the filling of the porosity by expansive iron corrosion products.

### 3.4 Discussion

The achieved experimental results and the proposed modelling show that there is a significant effect of the inner porosity of the pumice (system E). This effect is a clogging delay compared to the
Fe\textsuperscript{0}/sand system (Fig. 4). This result is explained by the internal porosity of pumice particles which may store iron corrosion products, delaying the filling of the inter-granular porosity. Although theoretically sound [58,65,66], this hypothesis has to be confirmed in future works, for instance, using X-ray micro-tomography to probe inner porosity of the pumice specimen and considering various pumice material with differential pore connectivity.

For a better understanding of the evolution of the initial porosity as iron corrosion proceeds, it is imperative to couple imaging (visualization) and mathematical modelling. The first attempt to visualize the deposition of iron particles (nano-scale) in the context of remediation with Fe\textsuperscript{0} was recently published [67]. It is expected that the use of X-ray microtomography visualization (and other appropriate techniques) will enable a better understanding of the effects of corrosion products on the bed clogging and to interpret the evolution of the residual porosity.

An increase of the sustainability of the Fe\textsuperscript{0} bed is noticed (Tab. 5). More iron could be consumed at the time $t_{\text{limit}}$. The extent of Fe\textsuperscript{0} depletion is increased by using admixtures. This result corroborates the view that admixing Fe\textsuperscript{0} with non-expansive material is a tool to induce sustainability [14,24]. Accordingly, the repeatedly reported cost reduction (Fe\textsuperscript{0} costs) ([21] and ref. cited therein) should be regarded as a positive side-effect. In other words, while using admixtures, material wastage [12] is avoided and service life is increased. It seems that the Fe\textsuperscript{0} proportion in efficient real systems should be lower than 50 % (1:1, v/v) used here [23,24]. In fact, the efficiently permeable reactive barrier at Borden (Ontario, Canada) contained only 22 % Fe\textsuperscript{0} (w/w) [1]. On the other hand, while testing Fe\textsuperscript{0} for viruses and bacteriophages removal from drinking, Shi et al. [68] found out that a sand filter containing only 15 % Fe\textsuperscript{0} (w/w) was very efficient for microbe removal. The design of Shi et al. [68] consisted in a column packed with sand (sand filter) containing a reactive Fe\textsuperscript{0}/sand layer (50:50, v/v). While the Fe\textsuperscript{0}/sand ratio was the same as the one discussed here, this work and related studies propose that parameters such as the characteristics of the column, the mass of Fe\textsuperscript{0}, the chemical reactivity of Fe\textsuperscript{0}, the thickness of the Fe\textsuperscript{0}/sand layer, the proportion of Fe\textsuperscript{0}, the relative
size of used particles ($\delta$ values), the porosity of the additives are routinely given to enable the comparison of results.

4 Conclusions

The concept that dual Fe$^0$/inert additive systems are more sustainable than pure Fe$^0$ systems for water treatment is validated using pumice and sand as additives and Cu$^{II}$, Ni$^{II}$ and Zn$^{II}$ as model contaminants. As expected the sand system was more efficient for contaminant removal and the pumice system more permeable. The order of contaminant removal efficiency corresponds to the selectivity sequence for iron oxides. This observation corroborates the view that chemical reduction (if applicable) is of secondary important for the process of contaminant removal.

The presented work highlights the volumetric expansive nature of iron corrosion as the most important clogging factor in water treatment. Filter clogging is demonstrated to be related to pore blocking in the inlet zone. Therefore, reliable strategies have to be developed to design sustainable Fe$^0$ filters under environmental conditions (water works). Systematic research at laboratory scale is needed to understand the impact of various factors on the clogging process. These factors include: the temperature, the nature of Fe$^0$ (chemical reactivity) and used additives (reactivity, porosity), the shape and dimension of Fe$^0$ and additives, the relative dimensions of Fe$^0$ and additives ($\delta$ values) and the quality of the inflowing aqueous solution (pH, O$_2$ level, HCO$_3^-$, humic substances, contaminants). The possibility to use various Fe$^0$ materials of different reactivity in the treatment chains should be carefully considered. For example, a readily reactive Fe$^0$ material (e.g. powdered) can be used in the first column(s) as O$_2$ scavenger and substituted when clogging occurs. In such a configuration, less reactive materials (e.g. granular) are used in subsequent columns for effective water treatment.

The net output of such a systematic research will be the minimization of uncertainties on the long term efficiency (sustainability) of Fe$^0$-based filtration systems, including nano-scale Fe$^0$. The lack of systematic approach has already led to difficulties in finding research funding [69] after more
than 15 years intensive research. Moreover, there is currently a hindrance in the spreading of this
efficient technology in Europe [70]. At the term, a small number of avoidable failures could result
in dismissal of a proven efficient technology.

Acknowledgements

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activity.

This paper is the results of the joint work of the authors.

References


[8] R.W. Gillham, Development of the granular iron permeable reactive barrier technology (good
science or good fortune). In "Advances in environmental geotechnics : proceedings of the
International Symposium on Geoenvironmental Engineering in Hangzhou, China,


Table 1: Variability of the operational conditions for column experiments as illustrated by the dimension of the column (H, D), the nature of contaminants (X), the nature of additives, the Fe$^0$ mass, and the relative dimension of particles ($\delta$).

<table>
<thead>
<tr>
<th>X</th>
<th>H (cm)</th>
<th>D (cm)</th>
<th>Additive</th>
<th>Fe$^0$ (g)</th>
<th>$d_{Fe}^{(*)}$ (mm)</th>
<th>$d_{additive}^{(*)}$ (mm)</th>
<th>$\delta^{(**)}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE, PCE</td>
<td>50</td>
<td>3.8</td>
<td>Sand</td>
<td>n.a.</td>
<td>0.25</td>
<td>1.315</td>
<td>0.19</td>
<td>[1]</td>
</tr>
<tr>
<td>As</td>
<td>31</td>
<td>2.5</td>
<td>Sand</td>
<td>75</td>
<td>0.42</td>
<td>0.275</td>
<td>0.65</td>
<td>[25]</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>30</td>
<td>5</td>
<td>Sand</td>
<td>1636</td>
<td>0.3</td>
<td>n.a.</td>
<td>(-)</td>
<td>[26]</td>
</tr>
<tr>
<td>Cr</td>
<td>10</td>
<td>2.5</td>
<td>Sand</td>
<td>n.a.</td>
<td>1.45</td>
<td>0.638</td>
<td>0.44</td>
<td>[27]</td>
</tr>
<tr>
<td>As</td>
<td>17.8</td>
<td>5.1</td>
<td>Sand</td>
<td>400</td>
<td>0.15</td>
<td>0.4</td>
<td>0.38</td>
<td>[28]</td>
</tr>
<tr>
<td>As</td>
<td>4</td>
<td>0.1</td>
<td>Sand</td>
<td>1.5</td>
<td>n.a.</td>
<td>0.5</td>
<td>(-)</td>
<td>[29]</td>
</tr>
<tr>
<td>Cu</td>
<td>45</td>
<td>5</td>
<td>Sand</td>
<td>525</td>
<td>0.7</td>
<td>0.8</td>
<td>0.88</td>
<td>[30]</td>
</tr>
<tr>
<td>TCE</td>
<td>40</td>
<td>1.59</td>
<td>Sand</td>
<td>80</td>
<td>1.355</td>
<td>0.118</td>
<td>0.09</td>
<td>[21]</td>
</tr>
<tr>
<td>As</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Sand</td>
<td>n.a.</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>[31]</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>20</td>
<td>2</td>
<td>Sand</td>
<td>90</td>
<td>0.1</td>
<td>0.55</td>
<td>0.19</td>
<td>[32]</td>
</tr>
<tr>
<td>Cu, Ni</td>
<td>50</td>
<td>5</td>
<td>Pumice</td>
<td>240</td>
<td>0.5</td>
<td>0.30</td>
<td>0.6</td>
<td>[33]</td>
</tr>
<tr>
<td>Cu, Ni, Zn</td>
<td>50</td>
<td>5</td>
<td>Sand</td>
<td>200</td>
<td>0.5</td>
<td>0.28</td>
<td>0.6</td>
<td>present</td>
</tr>
<tr>
<td>Cu, Ni, Zn</td>
<td>50</td>
<td>5</td>
<td>Pumice</td>
<td>200</td>
<td>0.5</td>
<td>0.30</td>
<td>0.6</td>
<td>present</td>
</tr>
</tbody>
</table>

(*) $d_{Fe}$ and $d_{additive}$ are the mean grain size of Fe$^0$ and the additive respectively.

(**) $\delta$ is the diameter ratio of the smaller particle size to the larger one (Fe$^0$ or additive).
**Table 2:** Characteristics of used materials tested by Mercury Intrusion Porosity (MIP).

<table>
<thead>
<tr>
<th></th>
<th>Fe$^0$</th>
<th>Pumice</th>
<th>Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific weight $\rho_s$ (g/cm$^3$)</td>
<td>7.78</td>
<td>1.92</td>
<td>2.60</td>
</tr>
<tr>
<td>Apparent specific weight $\rho_{as}$ (g/cm$^3$)</td>
<td>7.78</td>
<td>1.14</td>
<td>2.60</td>
</tr>
<tr>
<td>Compactness C(-)</td>
<td>0.51</td>
<td>0.45</td>
<td>0.55</td>
</tr>
<tr>
<td>Inter particular porosity $\Phi_{inter}$ (%)</td>
<td>49.6</td>
<td>54.8</td>
<td>45.0</td>
</tr>
<tr>
<td>Intra particular porosity $\varphi_{pp}$ (%)</td>
<td>-</td>
<td>41.0</td>
<td>-</td>
</tr>
<tr>
<td>Porosity $\Phi_0$ (%)</td>
<td>49.6</td>
<td>73.3</td>
<td>45.0</td>
</tr>
</tbody>
</table>
Table 3: Main characteristics of the studied columns. “rz_{eff}” is the measured reactive zone. The estimated porosity is also given.

<table>
<thead>
<tr>
<th>System</th>
<th>Media</th>
<th>Fe(^\circ)</th>
<th>Fe(^0)</th>
<th>Additive</th>
<th>Duration</th>
<th>rz(_{eff})</th>
<th>Porosity*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(vol %)</td>
<td>(g)</td>
<td>(g)</td>
<td>(days)</td>
<td>(cm)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>sand</td>
<td>0.0</td>
<td>0.0</td>
<td>1060</td>
<td>28</td>
<td>40.0</td>
<td>45.05</td>
</tr>
<tr>
<td>B</td>
<td>pumice</td>
<td>0.0</td>
<td>0.0</td>
<td>27</td>
<td>28</td>
<td>2.6</td>
<td>72.6</td>
</tr>
<tr>
<td>C</td>
<td>Fe(^0)</td>
<td>100.0</td>
<td>200</td>
<td>0.0</td>
<td>17**</td>
<td>2.6</td>
<td>49.6</td>
</tr>
<tr>
<td>D</td>
<td>Fe(^0) + sand</td>
<td>50.0</td>
<td>200</td>
<td>76.4</td>
<td>15**</td>
<td>5.2</td>
<td>46.05</td>
</tr>
<tr>
<td>E</td>
<td>Fe(^0) + pumice</td>
<td>50.0</td>
<td>200</td>
<td>27.0</td>
<td>28**</td>
<td>5.0</td>
<td>59.5</td>
</tr>
</tbody>
</table>

* In this values the internal porosity of the pumice is also included.

**-marked systems were stopped because of excessive permeability loss.
Table 4: Magnitude of contaminant removal in investigated systems.

<table>
<thead>
<tr>
<th>System</th>
<th>m_{in} (mg)</th>
<th>E (%)</th>
<th>E_s (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>A</td>
<td>685</td>
<td>685</td>
<td>927</td>
</tr>
<tr>
<td>B</td>
<td>685</td>
<td>685</td>
<td>927</td>
</tr>
<tr>
<td>C</td>
<td>367</td>
<td>367</td>
<td>497</td>
</tr>
<tr>
<td>D</td>
<td>367</td>
<td>367</td>
<td>497</td>
</tr>
<tr>
<td>E</td>
<td>612</td>
<td>612</td>
<td>828</td>
</tr>
</tbody>
</table>
Table 5: Modelled characteristics of Fe$^0$-containing columns. The extent of Fe$^0$ depletion (%) is given by: $\% \text{ consumed } \text{Fe} = 100 \frac{V_0 - V_t}{V_0}$ where $(V_0 - V_t)$ is the consumed Fe$^0$ volume with $V_0$ the initial volume of Fe$^0$ and $V_t$ its residual Fe$^0$ at time $t$.

<table>
<thead>
<tr>
<th>System</th>
<th>$t_{\text{limit}}$ (*)</th>
<th>Fe$^0$ depletion (%)</th>
<th>Fe$^0_{\text{residual}}$ (g)</th>
<th>$\Phi/\Phi_0$ (**)</th>
<th>$E_{s,\text{eff}}$ (mg/g) (***)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^0$</td>
<td>7.5</td>
<td>17.1</td>
<td>168.8</td>
<td>4.6</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe$^0$:sand</td>
<td>10.0</td>
<td>33.2</td>
<td>133.6</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Fe$^0$:pumice</td>
<td>16.0</td>
<td>41.4</td>
<td>117.2</td>
<td>1.4</td>
<td>4.3</td>
</tr>
</tbody>
</table>

(*) $t_{\text{limit}}$ is the time which corresponds to a constant hydraulic conductivity.

(***) $\Phi/\Phi_0$ is the residual porosity. $\Phi_0$ is the initial porosity of the column.

(***) $E_{s,\text{eff}}$ is the specific removal.
**Figure captions**

**Figure 1:** Schematic diagram of the experimental design. Used materials were (i) Fe\(^0\) (0 or 200 g), (ii) pumice (0 or 27 g), and (iii) quartz gravel (0 or 1060 g).

**Figure 2:** Time-dependant evolution of the pH value (a) and the iron concentration (b) of column effluent. The lines are not fitting functions, they simply connect points to facilitate visualization.

**Figure 3:** Magnitude of Cu (a), Ni (b), and Zn (c) breakthrough from the columns containing Fe\(^0\). The lines are not fitting functions, they simply connect points to facilitate visualization.

**Figure 4:** Time-dependant evolution of the hydraulic conductivity in the three systems containing Fe\(^0\) and the reference system pumice: (a) experimental K/K\(_0\) values; (b, c and d) relative permeability K/K\(_0\), experimental and modelled values. \(\eta = 6.4\), model 1: \(t_{\text{v,depletion}} = 50\) days, and model 2: \(t_{\text{v,depletion}} = 62.5\) days. For the three Fe\(^0\)-systems, the value at time \(t_{\text{limit}}\) has been adjusted so that the residual content of Fe\(^0\) is slightly superior to the Fe\(^0\) volume which is not consumed at clogging.