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# Reactive and hydraulic behavior of Permeable Reactive Barriers constituted by $Fe^0$ and granular mixtures of $Fe^0$/pumice

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**Abstract**

The objective of the present work is to analyze, by means of column tests, the reactivity and hydraulic long term behavior of the zero valent iron ($Fe^0$) and of a granular mixture $Fe^0$/pumice, for the remediation, through the Permeable Reactive Barriers technology, of nickel contaminated groundwater. The reactive behavior was studied by analyzing nickel concentration data, through a first order kinetic model in order to determine the thickness of a hypothetical PRB and its variation over time.
The hydraulic conductivity behavior was studied through a numerical-statistical geometrical model developed by the authors. Expansive iron corrosion, precipitation of reaction products and gas formation are the processes considered.

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*Keywords:* Column tests; nickel; hydraulic conductivity; statistical model

## 1. Introduction

A permeable reactive barrier (PRB) represents a valid technology for sustainable in situ remediation of contaminated groundwater. A PRB consists of a diaphragm wall, filled with a reactive material, installed perpendicularly to groundwater flow. When contaminated groundwater flows through the barrier, by means of its natural hydraulic gradient, chemical, physical or biological mechanisms occur [1].

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The zero valent iron ($Fe^0$) is usually used as reactive medium in PRB, but notwithstanding its high efficiency in contaminants removal, it can be inefficient in the long term because of its hydraulic behavior. The expansive nature of $Fe^0$ corrosion products, $H_2$ formation (derived by the anaerobic corrosion of $Fe^0$) and minerals precipitation are the possible causes of medium clogging. Admixing $Fe^0$ with a non-expansive material (e.g., gravel, $MnO_2$, pumice, and sand) is a possible solution to solve this problem [2].

In order to reach a target concentration down-stream a PRB the determination of its thickness is crucial. This parameter can be determined by interpreting column experiments data through a first order kinetic model as suggested by ITRC [1]. Another possible approach to determine barrier thickness is to calculate the removal capacity of the reactive material [1,3].

In this paper the reactive and hydraulic behavior of $Fe^0$ and of a granular mixture of $Fe^0$ and pumice was investigated through column tests. Long term column experiments have been carried out using $Fe^0$ alone and a granular mixture of $Fe^0$ and pumice (weigh ratio 30:70) and synthetic groundwater contaminated by nickel at initial contaminant concentrations of 8 mg/L (maintained constant for all tests duration).

The specific objectives of the present work are to determine: (1) thickness of the barrier using a first order kinetic model; (2) the difference in term of barrier thickness and lifespan between a barrier composed respectively by $Fe^0$ and by a granular mixture $Fe^0$/Pumice; (3) modelling the hydraulic behavior of the $Fe^0$ and a granular mixture of $Fe^0$/pumice through a numerical-statistical model.

## 2. Materials and methods

The used $Fe^0$ is of the type FERBLAST RI 850/3.5, distributed by Pometon S.p.A., Mestre, Italy. Whereas the used pumice originates from Lipari (Aeolian Islands, Sicily, Italy). The two materials are characterized by a uniform grain size distribution. The mean grain size ($d_{50}$) is approximately 0.5 mm and 0.3 mm for the two materials respectively. The $Fe^0$/pumice mixture was mixed at a weight ratio of 30:70. The contaminated aqueous solution was prepared by dissolving nickel(II) nitrate hexahydrate (purity 99.999) in distilled water in order to obtain initial concentration of 8 mg/L [4].

The experiments were carried out by using polymethyl methacrylate (PMMA—Plexiglas™) columns with an internal diameter of 5 ± 0.1 cm and a height of 50 cm, equipped with sampling ports located at different distances from the inlet (3, 8, 18, 28, 38 and 50 cm from inlet). The influent solution was pumped upwards from a single PE bottle by using a precision peristaltic pump (Ismatec, ISM930). A flow rate (Q) of 0.1 ml/min, corresponding to a Darcy velocity equal to 0.07 m/day, was used in order to simulate a possible in situ filtration velocity [4].

The aqueous concentrations of Ni was measured by using atomic absorption spectrophotometry (Shimadzu AA – 6701F). During the column tests, hydraulic conductivity was determined by using the falling-head or constant-head permeability methods [4].

The initial porosity ($n$) of the $Fe^0$/pumice mixture and of $Fe^0$ was estimated to be approximately 45% and 47% respectively, neglecting for the mixture the internal porosity of the pumice. A mass of 240 g of $Fe^0$ and 560 g of pumice was used to fill the entire height of the column (50 cm) whereas the column with $Fe^0$ was filled with 240 g up to a height of 3 cm and inert material (quartz gravel) was used to fill the remaining space [4].

## 3. Column tests results

The contaminant concentration (mass per unit volume) measured at each sampling port at time $t$ normalized respect to the influent concentration ($C_t/C_0$), can be plotted against the residence time for each sampling time and a first-order kinetic was hypothesized as follows:

$$\frac{C_t}{C_0} = e^{-k^* t} \tag{1}$$

where $k^*$ [$h^{-1}$] is the first-order kinetic coefficient. This parameter for the column test contained $Fe^0$ was determined using only two data: the initial concentration and the concentration evaluated at 3 cm of column length. Whereas for

the granular mixture, the first-order kinetic constant was determined considering the thickness of the reactive medium which contributes to the contaminant removal which varies during the test.

In Figure 1a the $k^*$ values obtained at each sampling time are plotted against time (h) for the column containing $Fe^0$ and the mixture $Fe^0$/pumice respectively. The value of $k^*$ decreases over time when $Fe^0$ is used, this decrease is less marked for the granular mixture (Fig. 1a).

Equation 1 can be rearranged to yield the time $T_r$ necessary to meet a target concentration ($C_{objective}$):

$$T_r = \frac{-\ln \frac{C_{objective}}{C_0}}{k^*} \tag{2}$$

The thickness of a PRB may be calculated based on site specific hydrogeology (i.e. seepage velocity $v_s$, the hydraulic gradient $dh/dl$ and hydraulic conductivity $k$) and the properties of the reactive medium (i.e. porosity $n$). The minimum barrier thickness for reaching target concentration $L$ can be therefore calculated with equation 3:

$$L = T_r \cdot v_s = T_r \frac{k\, dh/dl}{n} \tag{3}$$

Using the values of $k^*$ determined at each sampling time through equation 1 and considering a target concentration ($C_{objective}$) equal to 0.02 mg/L, as required by Italian Regulation [4].

Since the reactivity of the material decreases over time for a set lifespan of the reactive material, the thickness of the barrier can be determined as shown in Figure 1b for the two different reactive media ($Fe^0$ and the mixture $Fe^0$/pumice). The barrier thickness increases almost perfectly linearly over time when $Fe^0$ is used whereas for the granular mixture $Fe^0$/pumice the trend is still linear but with some fluctuations (Fig. 1b). The thickness of the $Fe^0$/pumice barrier varies from approximately 0.28 to 0.64 m for guaranteeing the target concentration for about 1 and 42 months respectively. The thickness of a $Fe^0$ barrier varies from approximately 0.04 to 0.06 m for a lifespan of respectively 1 and 8.5 months which is the duration of the column test before interruption due to an excessive hydraulic conductivity reduction [4]. Therefore the granular mixture is able to increase the lifespan of the barrier thanks to its ability to preserve hydraulic conductivity, that in fact still remains constant after more than three years.

## 4. Hydraulic conductivity modelling

In order to investigate the reactive medium long term hydraulic behavior a numerical-statistical geometrical model was proposed in the past by the authors. The model is derived by Simulfiltr, a theoretical method developed to simulate the filtration process inside granular soils in order to evaluate their internal stability [5,6].

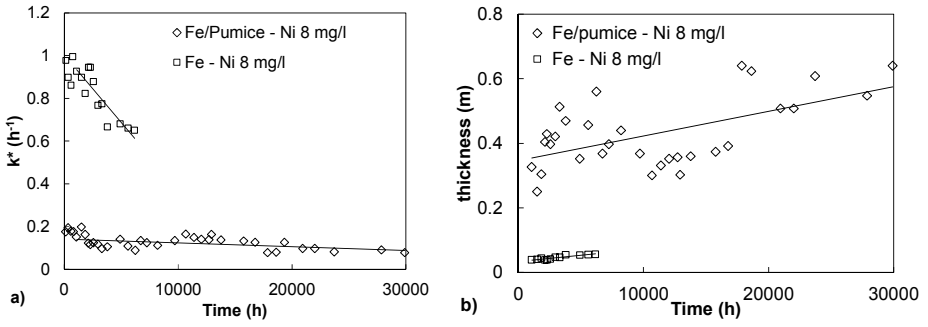


Fig. 1. Variation over time of (a) the kinetic constant; (b) of the barrier thickness for the $Fe^0$ and the mixture $Fe^0$/pumice.

The model proposed is described in detail in Moraci et al. [7] and refers to a reactive medium composed by $Fe^0$ alone. The model simulates the gas bubble movement, the expansion of iron grains due to corrosion and the precipitation of iron/contaminant compounds.

The reactive medium composed by $Fe^0$ granular particles (assumed spherical) is schematized by a sequence of parallel layers, placed upon each other at a distance, in the flow direction, equal to the $Fe^0$ mean grain size. The constrictions (the narrow throat that connects two pores) are created by the contact of four $Fe^0$ particles in different combinations. The constrictions size distribution is obtained applying the geometric stochastic method proposed by Silveira [8] and Silveira et al. [9] to the $Fe^0$ grain size distribution. The $Fe^0$ numerical grain size distribution is obtained from the soil weight grain size distribution considering relation of Musso and Federico [10]. In order to simulate the randomness of bubbles and constrictions positions, a sampling stochastic method on the cumulated numerical distribution of both the number and size of constrictions and bubbles is applied [7]. The simulation of gas bubbles movement is performed by comparing each bubble contained in the *i-th* layer with the constrictions contained in the next *(i + 1)-th* layer (Fig. 2a).

The volume of $Fe^0$ corrosion products $V_{iron\_corrosion\_products}$ was determined through the following law:

$$V_{iron\_corrosion\_products} = \eta \cdot V_{iron\_corroded} \tag{4}$$

where $V_{iron\_corroded}$ is the volume of iron consumed in the corrosion process and $\eta$ is the "rust expansion coefficient" which is assumed in the proposed model equal to 2.37 which is the average value calculated among the species detected during experimental activity i.e. Goethite $\eta = 2.91$, Hematite $\eta = 2.12$ and Magnetite $\eta = 2.08$ [7].

The iron expansion volume $V_{exp}$ can be calculated according equation 5:

$$V_{\exp} = (\eta - 1) \cdot V_{iron\_corroded} \tag{5}$$

The volume of iron corroded $V_{iron\_corroded}$ [$cm^3$] was determined through the iron corrosion rate *Iron_corrosion_rate,* considered a model calibration parameter (it is assumed that $Fe^0$ expansion is uniform for each particle), using eq. 6:

$$V_{iron\_corroded} = \frac{PM_{Fe^0}}{\rho_{Fe^0}} \cdot t \cdot Iron\_corrosion\_rate \cdot M_{Fe^0} \cdot 10^{-6} \tag{6}$$

where $PM_{Fe^0}$ and $\rho_{Fe^0}$ are the respectively the molecular weight [55.8 g/mol] and density [7.87 g/$cm^3$] of the $Fe^0$, $t$ is the time [day], $M_{Fe^0}$ is the mass of $Fe^0$ [g].

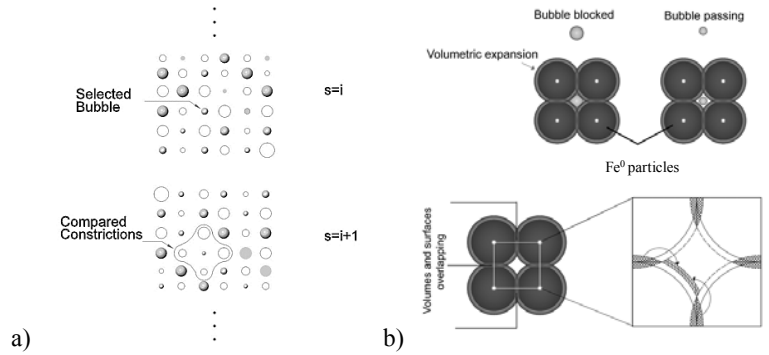


Fig. 2. (a) Scheme of comparison between bubbles and constrictions; (b) Schematization of bubbles blocked and passing and Set i-th of 4 particles and volume and surface overlapping (modified by [7]).

In anaerobic condition iron corrosion results in the formation of hydrogen according the following equation:

$$Fe^0 + 2H_2O \longrightarrow Fe^{2+} + H_2(g) + 2OH^- \quad (7)$$

In this reaction, 1 mole of hydrogen gas is generated for every mole of iron corroded by water. Knowing the mass of $Fe^0$, used in the column experiments, and the average iron corrosion rate, hydrogen production is calculated according to equations 7 and the ideal gas law. The average diameter of gas bubbles, depends by a number of factors (e.g. pressure and temperature) and it is considered a model calibration parameter. Gas bubbles are assumed spherical. The final volume of precipitates, generated during contaminant removal, was calculated knowing the mass of contaminant removed at the end of the tests (derived by a mass balance) and hypothesizing that Ni precipitates in the system as trevorite $Ni(Fe^{3+})_2O_4$, (density equal to 5.165 g/cm$^3$) as detected in previous studies [7]. It was hypothesized that the volume of precipitates increases linearly over time up to the final value.

Based on the Kozeny-Carman equation, the hydraulic conductivity $k$ can be calculated as:

$$k(t) = T_o \frac{n(t)^3}{(1-n(t))^2 M_s(t)^2} \quad (8)$$

Where $n(t)$ is the porosity interested by the contaminated solution flow at time $t$ (accessible porosity), $M_s(t)$ is the specific surface area at time $t$ (equation 9) and $T_0$ is a tortuosity parameter. For modelling purposes it was considered that the accessible porosity $n(t)$ decreases over time due to *i)* iron corrosion products *ii)* contaminant precipitates and *iii)* gas bubbles arrested in the overall reactive medium (since gas bubbles cannot be crossed by the contaminated solution they are considered as a solid having a own volume and surface which creates an obstruction to the flow). Therefore the effect of partial saturation, due to gas stopping, was considered as a reduction of accessible porosity in saturated soils.

The overlapping volume is supposed to be redistributed upon free surfaces (Fig. 2b). The presence of precipitates on $Fe^0$ surface was taken into account by considering a uniform redistribution of the volume of precipitates on the $Fe^0$ expanded surface. The specific surface $M_s(t)$ can be determined from equation 9:

$$M_s(t) = \frac{S(t)}{V_s(t)} \quad (9)$$

Therefore the specific surface changes over time due the surface variation of *i)* iron corrosion products, *ii)* precipitated contaminants and *iii)* arrested bubbles. An initial $Fe^0$ specific surface area equal to 0.17 m$^2$/g is used in the model [7]. Whereas $V_s(t)$ is the overall solid reactive medium volume including the volume of the *i)* iron corrosion products, *ii)* precipitated contaminants and *iii)* arrested bubbles.

It was necessary to simulate only the behavior of the first 1.5 cm of reactive medium (30 layer x 30 rows x 30 columns) because clogging is usually observed only at the entrance zone of $Fe^0$ systems [7].

Figure 3 shows the variation of hydraulic conductivity normalized respect to the initial value $k/k_0$ as function of time for the $Fe^0$ (Fig. 3a) and the mixture $Fe^0$/pumice (Fig. 3b). In the figures the values determined by means of permeability test and the results obtained using the new proposed model are showed. The two reactive media have a different hydraulic behavior, the granular mixture is able to preserve the hydraulic conductivity for a period greater than a barrier composed by $Fe^0$ alone, in fact for this latter the hydraulic conductivity decreases by five order of magnitude after 5906 h (about 8.5 months). Considering the hydraulic behavior of $Fe^0$ alone (Fig. 3a) when only $Fe^0$ expansion or $Fe^0$ expansion and precipitates formation are considered the variation of $k/k_0$ profiles are linear with time and model results are not able to fit the experimental values. When $Fe^0$ expansion, mineral precipitation and gas formation are considered the model is able to match in a more satisfactory way the hydraulic conductivity reduction observed in the column test [7]. According to model results hydraulic conductivity reduction could be due to gas stopping due to a reduction in constriction size (with dimension lower than average gas bubble diameter).

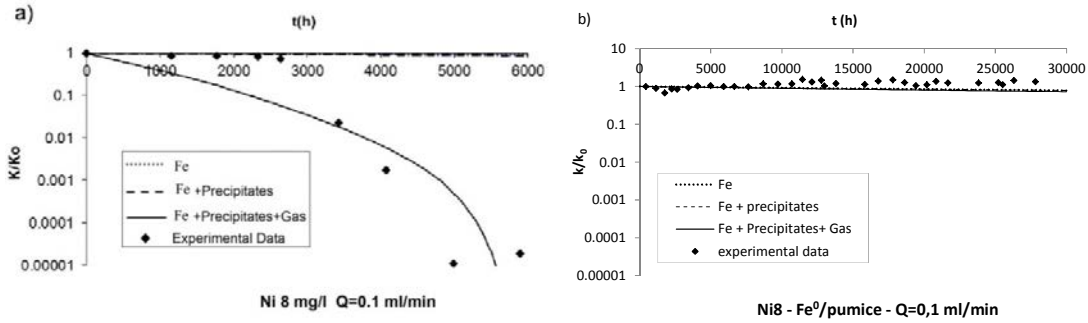


Fig. 3. Experimental data and model results of the ratio k/k0 as function of time for (a) Fe0 and (b) Fe0/pumice mixture.

The calibration parameters are the iron corrosion rate (1.2 mmol/kg*d), the average gas bubbles diameter (0.175 mm) and the standard deviation σ of its frequency distribution (0.01 mm). The discrete frequency distribution of the bubbles diameters is approximated by a Gaussian distribution characterized by a mean "μ", calibrated in order to fit the experimental results.

The model was modified for modelling the hydraulic conductivity of a granular mixture composed by two materials the $Fe^0$ and another material (in this case pumice). From the grain size distribution in weight of the mixture obtained from the grain size weight distribution of each material and taking into account the two different densities and the weight ratio, was obtained the numerical grain size distribution. In the case of a mixture of two soils the number of constrictions which are reduced are proportional to the ratio between the number of $Fe^0$ particles and the particles of the other granular material. The variation of the porosity and of the specific surface (eq. 9) takes into account this ratio. In the mixture $Fe^0$/pumice a decrease of hydraulic conductivity was not observed, the profiles obtained by the model and referred to the only $Fe^0$ expansion and to $Fe^0$ expansion and precipitates formation, are almost similar due to the negligible volume of precipitates compared to the volume of voids of the reactive medium, and the consequently negligible impact on the hydraulic conductivity (Fig. 3b). In order to fit experimental results in presence of gas, an average gas bubble diameter equal to 0.04 mm was considered, whereas the same value of the iron corrosion rate, calibrated in the previous simulation referred to $Fe^0$ alone, was maintained. A change of the gas bubble diameter, respect to the $Fe^0$ alone, can be due to the different grain size distribution and to the consequent variation of constrictions of the mixture and this change can have an impact on the size of individual gas bubbles [11].

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