Long-Term Efficiency of Zero-Valent Iron - Pumice Granular Mixtures for the Removal of Copper or Nickel From Groundwater

N. Moraci, P.S. Calabrò, P. Suraci

Abstract. The use of Permeable Reactive Barriers (PRBs) for in situ remediation of contaminated groundwater represents an attractive technology for both economic and operational reasons. A reactive medium widely used in PRBs is the Zero-Valent Iron (ZVI) which, in several case studies, has proved highly efficient for the removal of both inorganic and organic contaminants. One of the major concerns related to ZVI PRBs is their long-term hydraulic conductivity, which often decreases during operation, potentially compromising the long-term efficiency and durability of the barrier. This paper proposes the use of granular mixtures of ZVI and natural pumice in various weight ratios with the aim of solving this problem. The experimental research was carried out using two different metallic contaminants (nickel and copper) in aqueous solution at two concentrations. The issues related with long-term efficiency of the PRB are examined on the basis of the results of the experimental activity carried out by means of long-term column tests. It is demonstrated how iron-pumice granular mixtures are efficient in contaminant removal and, at the same time, are able to maintain constant the permeability of the PRB.

Keywords: contaminated groundwater, heavy metals, hydraulic conductivity, permeable reactive barrier, pumice, zero-valent iron.

1. Introduction

The use of Permeable Reactive Barriers (PRBs) for in situ remediation of contaminated groundwater represents an attractive technology both for economic and operational reasons (Thiruvenkatachari *et al.*, 2008; USEPA, 2004; NTUA, 2000; USEPA, 1998). A Permeable Reactive Barrier consists of a permeable subsurface wall composed of various reactive media, commonly built as a continuous trench filled with the treatment material. The trench is perpendicular to and intercepts the contaminated groundwater plume. As the water flows through it under the natural hydraulic gradient, the reactive medium degrades or traps the contaminants, providing the remediation of the aquifer by means of physical, chemical, biological or mixed processes. A PRB does not need any energy input, because it uses the natural hydraulic gradient of groundwater (passive method).

The reactive medium in the barrier interacts with the contaminants according to the above mentioned processes, removing (degrading or trapping) the pollutants and preventing the flux of the contaminants downstream of the PRB location. For the correct design of a PRB, a detailed geotechnical and hydrogeologic site characterization and an accurate physical and chemical study of the contamination are required in order to select the reactive medium and the barrier dimensions and configuration.

A filling reactive material widely used in PRBs is the Zero-Valent Iron (ZVI), which has demonstrated, in several cases presented in the scientific literature, a very good efficiency, in particular for heavy metals (*e.g.* Cd, Cr, Cu, Ni, Pb, Zn) removal (*e.g.* Wilkin and Mc Neil, 2003; Morrison *et al.*, 2002), even if it has been extensively and successfully used for the removal of other organic and inorganic compounds (*e.g.* Cundy *et al.*, 2008; Thiruvenkatachari *et al.*, 2008; Blowes *et al.*, 2000; NTUA, 2000; USEPA, 1998).

Notwithstanding its flexibility and good performance, the use of ZVI alone demonstrated some drawbacks regarding to the long-term efficiency of the PRB especially in terms of permeability (Li *et al.*, 2006; Li *et al.*, 2005; Liang *et al.*, 2005; Vogan *et al.* 1999; Mackenzie *et al.*, 1999), given its natural tendency for corrosion. In fact, the accumulation of precipitates (mainly hydroxides and salts such as carbonates) resulting from iron corrosion modifies the efficiency and especially the permeability of the barrier in time. Such a phenomenon can eventually lead to the generation of preferential paths towards zones outside the barrier (characterized by higher permeability), making the contaminated groundwater flow bypass the barrier itself.

N. Moraci, Mechanics and Materials Department, Faculty of Engineering, Mediterranean University of Reggio Calabria, Reggio Calabria, Italy. E-mail: nicola.moraci@unirc.it.
P.S. Calabrò, Mechanics and Materials Department, Faculty of Engineering, Mediterranean University of Reggio Calabria, Reggio Calabria, Italy. E-mail: paolo.calabro@unirc.it.
P. Suraci, Mechanics and Materials Department, Faculty of Engineering, Mediterranean University of Reggio Calabria, Reggio Calabria, Italy. E-mail: paolo.suraci@unirc.it.
Submitted on June 8, 2010; Final Acceptance on October 5, 2010; Discussion open until December 30, 2011.

The probability of this barrier bypass is increased by the recent trend of adopting semi-permeable funnels (hydraulic conductivity only two or three orders of magnitude lower than PRB) in funnel and gate configurations; in fact, in these conditions, if gate permeability decreases, the plume of contaminated groundwater can flow through the funnels.

Furthermore, when the barrier bypass is not possible, since the natural gradient of groundwater remains relatively constant, a decrease of hydraulic conductivity causes a parallel reduction of discharge through the barrier, significantly modifying the hydrogeology downstream.

In this paper, in order to sustain hydraulic conductivity in the long term and to optimize the use of ZVI, which is rather expensive, the adoption in PRBs of granular mixtures of zero-valent iron and pumice (a volcanic rock with a spongy, vitreous structure), in different weight ratios, is proposed.

The experimental research on the efficiency of ZVI-pumice granular mixtures in the removal of heavy metals was carried out by column tests, using an aqueous solution of the nitrates of two different metallic contaminants (nickel and copper) at various concentrations.

2. Contaminants Removal Mechanisms In Zero-Valent Iron Permeable Reactive Barriers

Iron (Fe) is a chemical element with three possible oxidation states: 0, +2 and +3 (other oxidation states are rare); ZVI acts as a reducing agent (electron donor) and tends to be easily and quickly oxidized (Fe^0/Fe^{2+} - E0 = -0,44 V), as outlined below, Fe^{2+} also, in certain conditions, can be further oxidized.

The groundwater contaminants passing through the barrier, if their redox potential is higher than - 0.44 V, act as electron acceptors and may be reduced.

For a generic metal (Me) the reactions involved are as follows:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \text{ oxidation}$$

$$Me^{2+} + 2e^- \rightarrow Me \text{ reduction}$$

Moreover, metallic contaminants may also be involved in reactions with other chemical compounds normally present in groundwater (*e.g.* carbonates, sulphides, hydroxides) forming solid precipitates. However, since the solubility of these compounds is strongly dependent on the pH value, the barrier should operate in a given pH range, so that the precipitates formed are barely soluble and are not re-transformed in a soluble form. At the same time the accumulation of precipitates in the barrier pores progressively reduce hydraulic conductivity (NTUA, 2000; Vogan *et al.* 1999; Mackenzie *et al.*, 1999).

If the ZVI oxidation takes place in anaerobic conditions (generally prevalent in groundwater) ferrous hydroxides are formed according to the following reactions:

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$\underline{Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

However, the rate of this reaction is slower than that involved in the removal of metallic cations (contaminants), while it is accelerated in aerobic conditions or when the metallic cations are removed from groundwater.

Furthermore, at high pH and high Fe^{2+}concentration, the ferrous ion will be further oxidized to the ferric state Fe^{3+}, precipitating as ferric hydroxide and potentially compromising the hydraulic conductivity of the barrier, according to the reaction:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$$

Therefore ZVI is easily corroded in an aqueous environment, even in the absence of contaminants; oxidation is not strictly detrimental to PRB performance, in fact, as a matter of fact, the contaminants reducing reactions imply ZVI corrosion.

Nevertheless, both iron corrosion and hydroxides formation have been generally believed to have a negative influence on the long-term effectiveness of the barrier, because corrosion implies a macroscopic dissolution of ZVI, thus reducing the reactive surface necessary to maintain contact with the contaminants, and because of the formation, on the reactive metal grains, of a thick layer of passivating oxidation products, the so-called “pseudo-protection” layer. According to the “traditional view” on ZVI PRBs, considering contaminants removal mainly due to oxidation-reduction reactions on the surface of ZVI grains, the presence of this “pseudo-protection” layer, preventing the water from coming into contact with virgin ZVI, prevents further oxidation of iron and subsequent reduction of metallic contaminants. A more complex mechanism for contaminants removal, directly involving corrosion products, has been recently proposed (Noubactep, 2008; Noubactep, 2006). According this new view, the heavy metals present in the contaminated solution are thus removed mainly through three possible processes (Noubactep, 2008; Noubactep, 2006; Rangsivek and Jekel, 2005; Wilkin and McNeil, 2003; Smith, 1996): reduction (direct reduction on the surface of ZVI or reduction through Fe^{2+} at the surface of corrosion products); adsorption onto corrosion products; and coprecipitation (precipitating corrosion products that can capture contaminants into their structure). Therefore contaminants removal is possible in three different places: on the ZVI surface, within the corrosion products film and on the surface of corrosion products.

According to Smith (1996), the SiOH sites that are present on the pumice surface are also able to remove the metals from the solution according to the reaction:

$$> SiOH + Me^{2+} \leftrightarrow (> SiO^{-} - Me^{2+})^{+} + H^{+}$$

where > represents the pumice surface.

Another mechanism for the removal of metals by pumice is the ionic exchange with alkaline and alkaline-earth metals present in the pumice structure. In fact according to information provided by the supplier of the pumice (Pumex spa, 2008) the bonds – Si – O–Me, where Me is an alkaline or alkaline-earth metal, are easily hydrolyzed to form the active group – Si – OH. Moreover, according to the results of the research activity carried out on the ZVI/Pumice granular mixtures (Moraci *et al.* 2010) it seems that Pumice can enhance ZVI performance due to its capacity of storing corrosion products in its pores thus augmenting the available reactive surface for the reactions and, at the same time, allowing the preservation of the hydraulic conductivity.

3. Materials and Methods

Pumice is a volcanic rock with a spongy, vitreous structure, characterized by a high internal porosity due to the expansion of magmatic gases during the effusion process by which it was generated. The pumice used in this research comes from the quarries of Lipari (Aeolian Islands, Sicily – Italy); it is a natural complex silicate (Pumex spa, 2008) constituted mainly by silica (SiO_2 – 71.75%) and by oxides of various elements (*e.g.* Al_2O_3 – 12.33%, K_2O – 4.47%, Na_2O – 3.59%, Fe_2O_3 – 1.98%, MgO – 0.12%, TiO_2 – 0.11%, MnO – 0.07%, FeO – 0.02%). In terms of morphology, the pumice presents irregularly shaped grains; three different grain size distributions were tested in the present research.

The average micropore diameter of pumice grains is lower than 5 μm (Rigano, 2007).

Pumice is generally considered chemically inert, since it is insoluble both in water and in acids or bases, except hydrofluoric acid (HF); it has, as already mentioned, a significant surface chemical activity due to the presence of – OH groups and mono and polyvalent ions in its chemical structure; therefore this material is able to form chemical bonds with organic and inorganic compounds. The pumice from Lipari with two different grain size distributions (called 16/40 and 2B) was used (Fig. 1). The uniformity coefficients, $C_u = D_{60}/D_{10}$, are, respectively, equal to 2.2 (Pumice 16/40) and 1.8 (Pumice 2B). The solid's unit weight, ρ_s, determined on the non-crushed grains of pumice was, respectively, equal to 16 kN/m^3 (Pumice 16/40) and 20 kN/m^3 (Pumice 2B). The same measurements carried out after the grains crushing revealed a solid's unit weight equal to 26 kN/m^3. The difference between the values is due to the internal porosity of pumice.

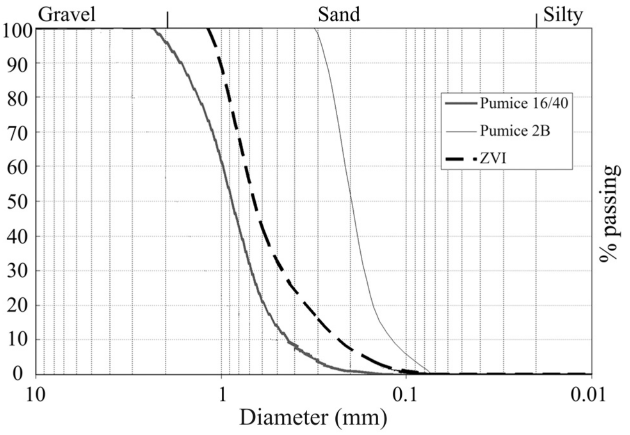

Figure 1 - Grain size distribution curves for Pumice and ZVI.

The ZVI used in this research is of the type FERBLAST RI 850/3.5, distributed by Pometon S.p.A., Mestre – Italy. The powder is composed mainly of ZVI (> 99.74%), with impurities constituted mainly of Manganese (about 0.26%) and traces of oxygen, sulphur and carbon. The grain size distribution is almost uniform (see Fig. 1) and the specific weight is of 78.5 kN/m^3 and the uniformity coefficients C_u is 2.4.

The solutions used in the column tests were obtained by mixing either copper nitrate or nickel nitrate with distilled water (Nickel(II) nitrate hexahydrate, purity 99.999; Copper(II) nitrate hydrate, purity 99.999; Sigma-Aldrich).

The assessment of the contaminant concentrations in the samples collected during the column tests was carried out by Atomic Absorption Spectrophotometry (AAS – Shimadzu AA – 6701F – method CNR-IRSA Q.no 64).

To evaluate the performance of the ZVI-Pumice granular mixtures column tests were carried out by letting a contaminated solution to flow through a polymethyl methacrylate (PMMA – Plexiglas) column (internal diameter = 5 cm; height = 100 cm) filled with the reactive medium. Each column had 9 sampling ports (Fig. 2), in correspondence with, respectively, the inlet and the outlet and the other 7 in between (*i.e.* 3, 8, 18, 28, 38, 58, 78 cm from the inlet).

The columns tests were performed with a constant upward flow (equal to 0.5 mL/min) using either a copper or a nickel solution. The constant flow was maintained during the test by using a precision peristaltic pump (Ismatec ISM 930). Five reactive media were used: ZVI; Pumice 16/40; three granular mixtures of ZVI and Pumice 2B (50:50, 30:70 and 10:90 weight ratio respectively). Pumice 2B was selected for granular mixtures according to the results of preliminary batch tests (not reported in this paper). The experimental program and the main characteristics of the different tests are reported in Table 1.

To assess the capacity of the mixtures to maintain an adequate long-term permeability, in the column tests carried out using the 10:90 ZVI-Pumice granular mixture, hydraulic conductivity was measured by constant head permeability tests. To make a direct comparison of the hydraulic performance of respectively ZVI and ZVI-Pumice granular mixture PRBs, the hydraulic conductivity was also

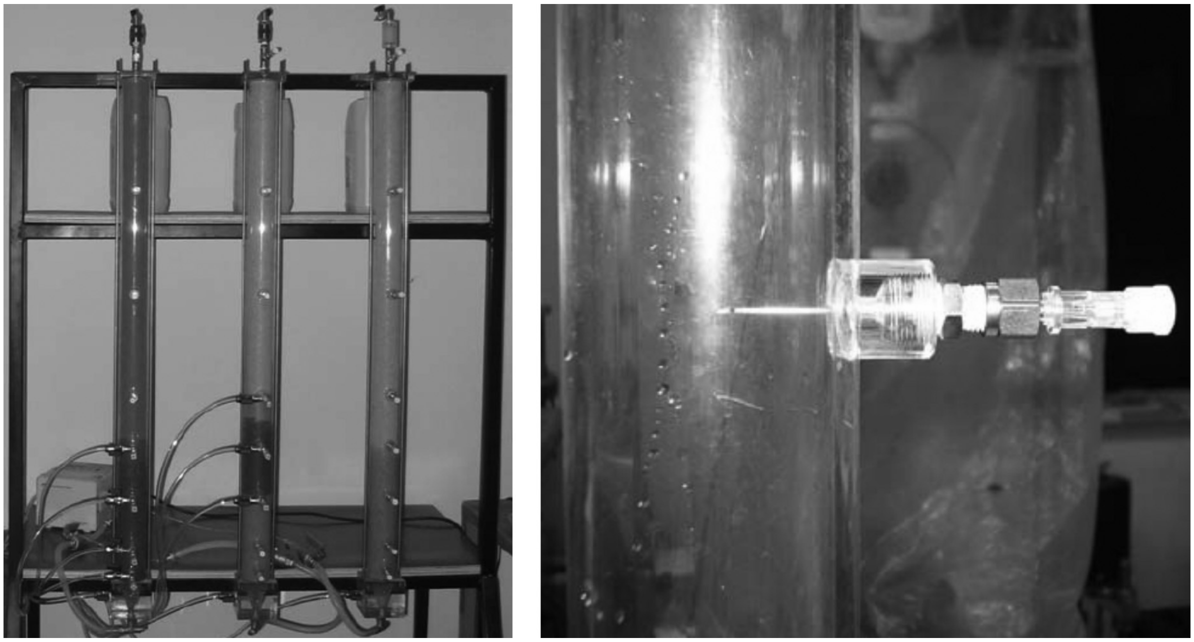

Figure 2 - Columns tests setup.

Table 1 - Column tests experimental program.

Contaminant	Initial concentr. (mg/L)	Reactive medium	Limit conc. Groundwater (mg/L)	ZVI (g)	Pumice (g)	PV (L)
Copper	50	ZVI	1	7850	-	0.97
Copper	50	Pumice 16/40	1	-	1015	1.33
Copper	50	ZVI-Pumice 2B; Weight Ratio 50:50	1	1240	1240	1.18
Copper	50	ZVI-Pumice 2B; Weight Ratio 30:70	1	595	1387	1.19
Copper	500	ZVI-Pumice 2B; Weight Ratio 10:90	1	155	1395	1.25
Nickel	5	ZVI	0.02	7850	-	0.97
Nickel	5	ZVI-Pumice 2B; Weight Ratio 50:50	0.02	1240	1240	1.18
Nickel	5	ZVI-Pumice 2B; Weight Ratio 30:70	0.02	595	1387	1.19
Nickel	40	ZVI-Pumice 2B; Weight Ratio 10:90	0.02	153	1374	1.26

measured in two columns filled with ZVI only and fed with the same contaminated solution of the 10:90 ZVI-Pumice granular mixture columns (see Table 1). Aqueous samples for chemical analyses were not collected from iron filled columns since they were used only as a benchmark for hydraulic conductivity tests.

In order to have a better understanding of the chemical mechanisms involved in the heavy metal removal, at the end of the test carried out on the columns filled with a granular mixture of ZVI and Pumice (weight ratio 10:90), a sample of the reactive medium was collected from the column inlet zone, the iron was magnetically separated from pumice and the two materials were dried in nitrogen atmosphere to prevent further reaction with the oxygen in the air. Nevertheless it was impossible to avoid air contact completely, especially during the extraction from the column, the drying and the preparation of the samples for the analyses. Furthermore, microscopic observation showed small pumice grains merged on the surface of iron grains while pumice samples appeared free of any iron inclusion.

Samples were analyzed using X-ray diffraction (XRD – Bruker D8 ADVANCE) and X-ray fluorescence (XRF – Bruker S2 RANGER).

4. Analysis of Experimental Results

The column tests results are shown in Table 2 and in Figs. 3 to 9. In particular, Figs. 3 to 6 present the tests results in terms of relative concentration (C/C_0, where C is the measured contaminant concentration in the samples collected and C_0 is the contaminant concentration at the inlet),

Table 2 - Column tests results.

Contaminant/ Initial conc.(mg/L)/ Reactive m.	Test duration (h)	Pollutant mass flowed (g)	Massic discharge (mg/s)	C_F (mg/L)	Specific removal (g cont./ g reac.m.)	Mass removal
Copper / 50 / ZVI	1032	1.548	$4.17*10^{-4}$	0.004	$1.97*10^{-4}$	99.993%
Copper / 50 / Pumice 16/40	528	0.792	$4.17*10^{-4}$	50*	$2.49*10^{-4}$§	18.970%
Copper / 50 / Mix ZVI-Pumice 2B; W. Ratio 50:50	1032	1.548	$4.17*10^{-4}$	0.007	$1.25*10^{-3}$	99.981%
Copper / 50 / Mix ZVI-Pumice 2B; W. Ratio 30:70	1032	1.548	$4.17*10^{-4}$	0.04	$2.6*10^{-3}$	99.901%
Copper/ 500 / Mix ZVI-Pumice 2B; W. Ratio 10:90	1500	22.555	$4.17*10^{-3}$	0.5	$1.45*10^{-2}/1.19*10^{-1}$§§	99.776%
Nickel / 5 / ZVI	1032	0.155	$4.17*10^{-5}$	0.002	$1.97*10^{-5}$	99.945%
Nickel / 5 / Mix ZVI-Pumice 2B; W. Ratio 50:50	1032	0.155	$4.17*10^{-5}$	0.003	$6.24*10^{-5}$	99.997%
Nickel / 5 / Mix ZVI-Pumice 2B; W. Ratio 30:70	1032	0.155	$4.17*10^{-5}$	0.005	$7.81*10^{-5}$	99.995%
Nickel/ 40 / Mix ZVI-Pumice 2B; W. Ratio 10:90	1500	1.612	$3.33*10^{-4}$	37.14**	$3.65*10^{-4}/5.19*10^{-4}$§§	30.759%

* Minimum concentration during the test equal to2.0 mg/L (measured at the outlet for T = 24 h).
** Minimum concentration during the test equal to 0.3 mg/L (measured at the outlet for T = 80,75 h).
§ Limit removal.
§§ Limit removal calculated for the sampling port at 8 cm from the inlet.

in time for ZVI-Pumice granular mixtures (weight ratio 30:70 and 10:90) for copper and nickel. Figures 7 and 8 show the trend of the contaminant specific mass removal (mass of contaminant removed for each gram of reactive medium) for the tests carried out using a granular mixture with a weight ratio of 10:90 for copper and nickel respectively. Figure 9 shows the variation in the hydraulic conductivity for the tests carried out using either the ZVI/Pumice granular mixture (weight ratio 10:90) or ZVI only.

The column tests results confirmed that granular mixtures of ZVI and Pumice, in different weight ratios (excepting the 10:90 granular mixture for nickel) have a significant remediation capacity for groundwater contaminated by either copper or nickel, reaching results both in terms of concentration and mass removed at the outlet of the column comparable (concentrations and mass removal at the outlet of the column are in the same order of magnitude) to those of the columns containing ZVI only but using a significantly lower amount of this reagent (see Table 2). In all columns tests the final pollutant concentration (C_F) reached values well below the limit stated in the Italian Regulation (Gazzetta Ufficiale della Repubblica Italiana, 2006); the only exception being constituted by the tests carried out using pumice alone or a granular mixture 10:90 and 40 mg/L nickel (Table 2), due, in the former, to the limited pumice efficiency and in the latter to the high contaminant concentration. The performance of granular mixtures with 30:70 and 50:50 weight ratio is very similar notwithstanding the higher ZVI content of the latter.

In the test carried out using a 50 mg/L Copper solution or a 5 mg/L Nickel solution (Figs. 3 and 4), both for the column using only ZVI as reactive medium and the mixture between ZVI and Pumice (weight ratio 30:70), the contaminant was almost completely removed in the first 3 cm of the column (Fig. 10). This circumstance is due to the fact that the mass of ZVI used in the columns greatly exceeds the amount necessary to remove the mass of contaminant flowing through the column during the test and to achieve the desired final concentration. This fact is proven by the evident corrosion only of the first layers of the filling material of the column, up to the first sampling port.

The fact that Figs. 3 and 4 present a steady trend is due to the limited duration of the transient period of the reaction that was probably already completed before the first sampling.

Table 2 clearly shows that the removal capacity of the pumice is limited and not sufficient alone to remedy severe contamination; in fact the column removal capacity was already exhausted after 528 h without reaching the allowed limit concentration.

The column tests carried out using ZVI-Pumice granular mixtures with weight ratio of 10:90 and highly contaminated solutions (Copper 500 mg/L and Nickel 40 mg/L, see Figs. 5 and 6) allowed the complete exhaustion of the reactive medium and the possibility to calculate the limit re-

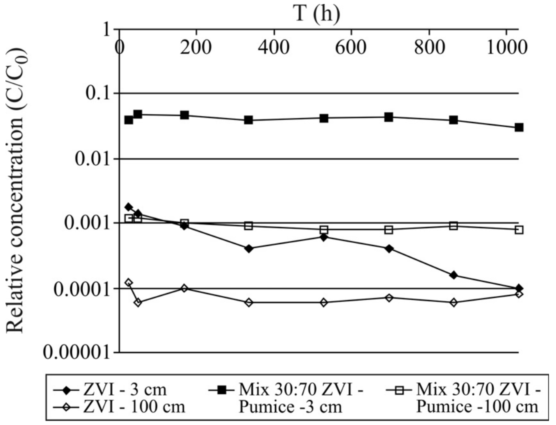

Figure 3 - Relative concentration *vs.* time for Copper (C_0 = 50 mg/L) in column tests with ZVI and ZVI – Pumice 2B granular mixture (weight ratio 30:70).

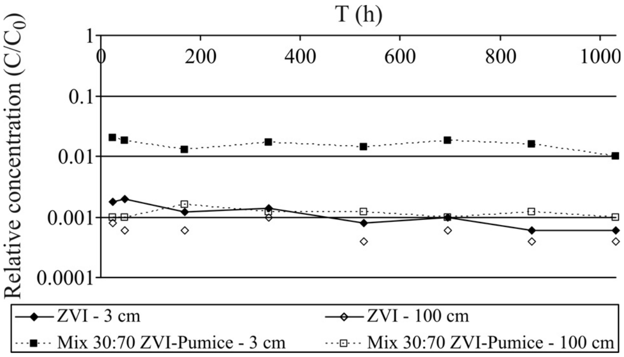

Figure 4 - Relative concentration *vs.* time for Nickel (C_0 = 5 mg/L) in column tests with ZVI and a ZVI – Pumice 2B granular mixture (weight ratio 30:70).

moval capacity. In particular, during the column test the removal capacity of the first 8 cm of the column solution tested with copper and nickel was completely annulated after respectively about 1200 and about 1000 h. The limit removal capacity of the reactive medium calculated for both the columns with reference to the first 8 cm differs for the two contaminants by more than two orders of magnitude (see Table 2), being higher for copper. Also, the trend of removal for the two pollutants is significantly different (Figs. 5 and 6).

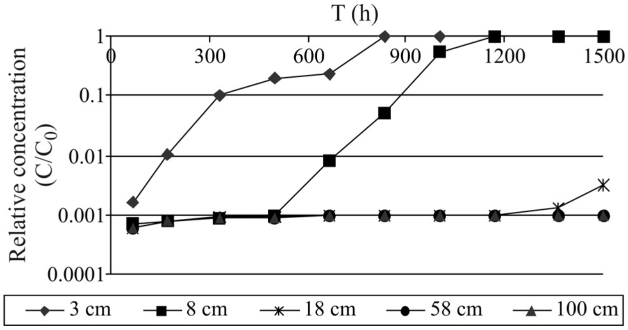

Figure 5 - Relative concentration *vs.* time for Copper (C_0 = 500 mg/L) in column test with a ZVI – Pumice 2B granular mixture (weight ratio 10:90).

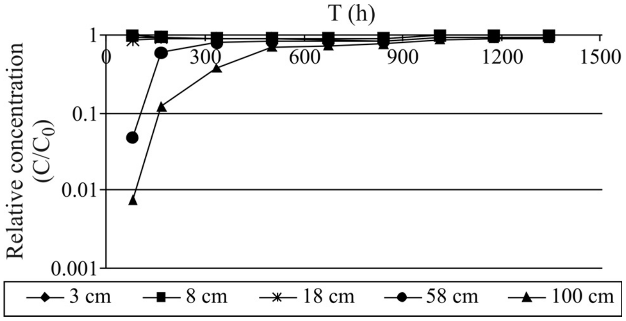

Figure 6 - Relative concentration *vs.* time for Nickel (C_0 = 40 mg/L) in column test with a ZVI – Pumice 2B granular mixture (weight ratio 10:90).

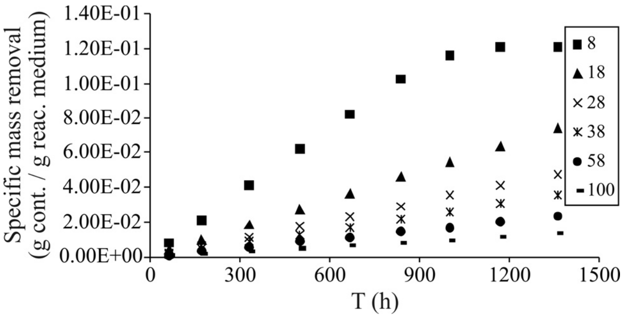

Figure 7 - Contaminant specific Mass Removal *vs.* time for Copper (C_0 = 500 mg/L) in column test with a ZVI – Pumice 2B granular mixture (weight ratio 10:90).

The column removal capacity for copper (Fig. 7) was progressively exhausted and the separation between the part of the column involved in the removal and the zone still potentially active, indicated by the pollutant concentration and by the trend of specific removal is clear. On the other hand, the trend observed for nickel is different: after only 168 h of test duration the pollutant concentration at the outlet of the column was of the same order of magnitude as the one at the inlet, although more than 50% of the length of the column was still clearly active (pollutant concentration lower than 80% of the inflowing pollutant concentration and high residual specific removal capacity, Fig. 8). The different behaviors of the ZVI/Pumice granular mixtures concerning the two contaminants (see Table 2) might be linked to different removal mechanisms and chemical kinetics, in fact copper is more efficiently and rapidly removed than nickel.

As already mentioned, in order to assess the long-term hydraulic behavior of the different reactive media, the hydraulic conductivity was measured during column tests carried out in columns filled with a ZVI-Pumice 2B - 10:90 granular mixture and with ZVI only respectively, and flushed with contaminated solutions having a concentration of either 40 mg/L of nickel or 500 mg/L of copper (Fig. 9).

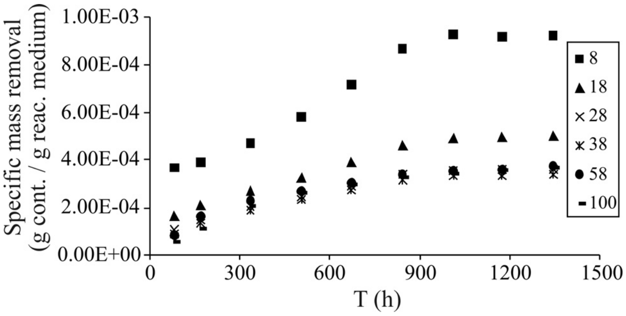

Figure 8 - Contaminant specific Mass Removal *vs.* time for Nickel (C_0 = 40 mg/L) in column test with a ZVI – Pumice 2B granular mixture (weight ratio 10:90).

At the beginning of the test the hydraulic conductivity was about 10^{-4} m/s for all the columns. At the end it was of the same order of magnitude (10^{-4} m/s) for the columns filled with the ZVI-Pumice mixture and for the one filled with ZVI only and flushed with the nickel contaminated solution, while it was more than four order of magnitude lower for the same column flushed with copper solution. This difference could be very probably be ascribed to the superior production of corrosion products in the column flushed with copper solution due to both the higher initial contaminant concentration and to the probable remarkable production of $Fe(OH)_3$ after complete metal removal (Moraci et. al., 2010). In fact, as already mentioned, metal removal and oxidation by water are probably competitive processes: the first is favored but when metal is removed the ZVI oxidation by water increases the pH and the related production of $Fe(OH)_3$ that precipitating increases clogging.

These results confirmed the efficiency of the granular mixtures in maintaining the hydraulic conductivity of the barrier in the long term while those filled with ZVI only present severe clogging problems (Fig. 9).

To give a more detailed analysis of the chemical mechanisms involved in contaminant removal, the results of XRD and XRF (Jeen *et al.*; 2007: Komnitsas *et al.*, 2007; Noubactep *et al.*, 2006; Rangsivek and Jekel, 2005; Furukawa *et al.* 2002) analyses carried out on the specimens from the samples collected from the columns after the test and on the same virgin materials are discussed below.

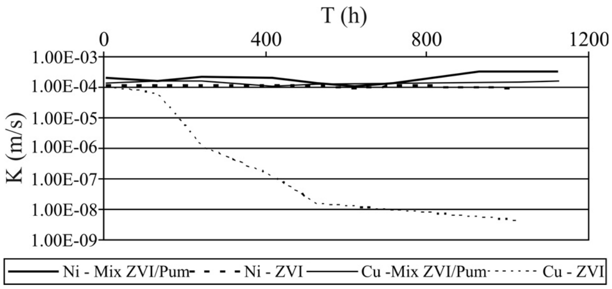

Figure 9 - Hydraulic conductivity *vs.* time in column test carried out using a either a ZVI – Pumice 2B granular mixture (weight ratio 10:90) or ZVI only and either Copper (500 mg/L) or Nickel (40 mg/L) contaminated solutions.

XRD tests allowed recognition of the crystalline compounds found in the iron and pumice specimens. The tests highlighted the presence of magnetite as the main oxidized form of ZVI; moreover, in the iron samples from the column fed with nickel, trevorite ($NiFe_2O_4$) was detected, while the presence of peaks due to traces of metallic nickel and bunsenite (NiO) cannot be confirmed with certainty. The presence of trevorite could be related to the coprecipitation of nickel and iron hydroxides (Pishch and Radion, 1996).

In the iron specimens collected from the column fed with copper, the main reaction products identified were copper hydroxide nitrate ($Cu_2(OH)_3NO_3$) and cuprite (Cu_2O); also in this case the presence of peaks due to trace of metallic copper cannot be confirmed. It is probable that cuprite derives from the oxidation, during sample preparation (pulverization by a mill), of Cu^0.

The XRD test carried out on pumice coming from the column fed with nickel does not reveal anything relevant, while the test carried out on the pumice taken from the copper column presents peaks attributable to copper hydroxide nitrate ($Cu_2(OH)_3NO_3$) and cuprite (Cu_2O).

The composition of the pumice samples given by XRF analyses is shown in Table 3; in the table, only compounds or elements present in concentrations higher than 1% have been reported since below this percentage the results are probably unreliable; however, the concentration of heavy metals present in the contaminated solution has been always reported.

From the analysis of these data, a rise in the concentration of iron and of the contaminant used during the test (copper or nickel, respectively) is evident. This fact is attributable to the contaminants removal performed by pumice and represents another demonstration that this material has a non negligible reactivity. The increase in iron concentration is similar for the two tests, while it seems that copper is more easily removed from the contaminated solution than nickel; nevertheless the concentration of the latter is

Table 3 - XRF analyses: Pumice composition after column tests using ZVI – Pumice 2B granular mixture (weight ratio 10:90) and Copper 500 mg/L and Nickel 40 mg/L contaminated solutions.

Compound	Pumice (contaminated solution Cu 500 mg/L)	Pumice (contaminated solution Ni 40 mg/L)
SiO_2	66.3%	69.9%
Cu	6.0%	-
Fe_2O_3	2.6%	3.4%
Al_2O_3	12.0%	12.6%
K_2O	4.0%	4.4%
Na_2O	5.8%	6.1%
MgO	2.0%	2.0%
Ni	-	0.3%

Figure 10 - ZVI filled column after the test.

only indicative, being close to the instrumental detection limit.

XRF analyses show that the amount of copper detected on the pumice sample is about 10% of that detected on the iron sample while for nickel this percentage is reduced to about 5%. This fact leads to the conclusions that for the 10:90 granular mixture flushed with copper contaminated solution, the removal imputable to ZVI is probably similar to the one imputable to Pumice, while for nickel it is approximately 50%. Moreover, it is likely that the amount of iron and contaminants found on pumice samples is also partly attributable to the accumulation of reaction products in the porous structure of pumice.

5. Conclusions

In this paper, in order to solve the problems related to the long term efficiency of ZVI PRBs in terms of permeability, the use of granular mixtures, in different weight ratios, of ZVI and pumice, a material never tested before for use in PRBs, has been proposed. The results of preliminary column tests, carried out using two different metallic contaminants (nickel and copper) in aqueous solution at different concentrations have been described, demonstrating that:

° The columns filled with iron-pumice mixtures presents a contaminant removal efficiency comparable to those filled with ZVI only;

° The most efficient compromise between efficiency (high metal removal) and efficient use of ZVI seems to be given by the granular mixture with 30:70 weight ratio.

° The permeability tests carried out during long term column tests using ZVI only, confirmed the possibility of problems related to PRBs clogging;

° The permeability tests carried out on the granular mixtures (ZVI-Pumice) confirmed the long term hydraulic efficiency of this material for use in PRBs and its capacity to maintain the aquifer flow.

Acknowledgments

The authors wish to thank Dott. Giuseppe Panzera (Ph. D.), Ing. Giulia Rigano (Ph. D.), and Ing. Stefania Bilardi (M. Sc.) for the indispensable help given during the research activity and to the Director and the Officials of the Environmental Protection sector of the Province of Reggio Calabria for the authorization to use the Atomic Absorption Spectrophotometer, property of the same Province.

References

Blowes, D.W.; Ptacek, C.J.; Benner, S.G.; McRae, C.W.T.; Bennett, T.A. & Puls, R.W. (2000) Treatment of inorganic contaminants using permeable reactive barriers. Journal of Contaminant Hydrology, 45:1-2, p. 123-137.

Cundy, B.; Hopkinson, L. & Whitby, R.L.D. (2008) Use of iron-based technologies in contaminated land and groundwater remediation: A review. Science of The Total Environment, v. 400:1-3, p. 42-51.

Furukawa, Y.; Kim, J.; Watkins, J. & Wilkin, R.T. (2002) Formation of ferrihydrite and associated iron corrosion products in permeable reactive barriers of zero-valent iron. Journal of Environmental Science and Technology, v. 36, p. 5469-5475.

Gazzetta Ufficiale della Repubblica Italiana (2006) Norme in materia ambientale (Environmental regulations). Gazzetta Ufficiale n. 88 del 14 aprile 2006. Poligrafico dello Stato, Roma.

Jeen, S.; Jambor, J.; Blowes, W. D. & Gillham, R. (2007) Precipitates on granular iron in solutions containing calcium carbonate with trichloroethene and hexavalent chromium. Journal of Environonmental Science and Technology, v. 41 p. 1989-1994.

Komnitsas, K.; Bartzas, G.; Fytas, K. & Paspaliaris, I. (2007) Long- term efficiency and kinetic evaluation of ZVI barriers during clean-up of copper containing solutions. Minerals Engineering, 20 p. 1200-1209.

Li, L.; Benson, C.H. & Lawson, E.M. (2006) Modeling porosity reductions caused by mineral fouling in continuous-wall permeable reactive barriers. Journal of Contaminant Hydrology, v. 83:1-2, p.89-121.

Li, L.; Benson, C.H. & Lawson, E.M. (2005) Impact of mineral fouling on hydraulic behavior of permeable reactive barriers. Ground Water, v. 43:4, p. 582-596.

Liang, L.; Moline, G.R.; Kamolpornwijit, W. & West, O.R. (2005) Influence of hydrogeochemical processes on zero-valent iron reactive barrier performance: A field investigation. Journal of Contaminant Hydrology, v. 78:4, p. 291-312.

Mackenzie, P.; Horney, D. & Sivavec, T. (1999) Mineral precipitation and porosity losses in granular iron columns. Journal of Hazardous Materials, v. 68:1-2, p. 1-17.

National Technical University of Athens (2000) Literature Review: Reactive Materials and Attenuation Processes for Permeable Reactive Barriers. Project on Long Term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated Groundwater. Project Contract Number: EVK1-CT-1999-00035. Web Site: www.perebar. bam.de.

Moraci, N.; Calabrò, P.S. & Bilardi, S. (2010) Efficiency of zero valent iron/pumice granular mixtures in simultaneous removal of copper and nickel. Proceedings of Hazardous and Industrial Waste Management Conference, Chania.

Morrison, S.J.; Metzler, D.R. & Dwyer, B.P. (2002) Removal of As, Mn, Mo, Se, U, V and Zn from groundwater by zero-valent iron in a passive treatment cell: reaction progress modelling. Journal of Contaminant Hydrology, v. 56:1-2, p. 96-116.

Noubactep, C. (2006) Contaminant reduction at the surface of elemental iron: the end of a myth. Wissenschaftliche Mitteilungen, v. 31, p. 173-179.

Noubactep, C. (2008) A critical review on the mechanism of contaminant removal in Fe0-H_2O systems. Environmental Technologies, v. 29:8, p. 909-920.

Noubactep, C.; Schoner, A. & Meinrath, G. (2006) Mechanism of uranium removal from the aqueous solution by elemental iron. Journal of Hazardous Materials B, v. 132, p. 202-212.

Pishch, I.V.; Radion, E.V. (1996) A pigment based on coprecipitated iron(III) and nickel(II) hydroxides. Glass and Ceramics, v. 53:6, p.178-179.

Pumex spa (2008) Lipari Pumice. Website http://www.pumex.it/pumex%20inglese.pdf. Accessed October 1, 2008.

Rangsivek, R.& Jekel, M.R. (2005) Removal of dissolved metals by zero-valent iron (ZVI): Kinetics, equilibria, processes and implications for stormwater runoff treatment. Water Research, v. 39, p. 4153-4163.

Rigano, G. (2007) Studio dell'efficienza di Barriere Permeabili Reattive per la bonifica di acquiferi contaminati da metalli pesanti. Ph. D. Thesis Università degli Studi Mediterranea di Reggio Calabria.

Smith, E.H. (1996) Uptake of heavy metals in batch systems by a recycled iron-bearing material. Water Research, v. 30:10, p. 2424-2434.

Thiruvenkatachari, R.; Vigneswaran, S. & Naidu, R. (2008) Permeable reactive barrier for groundwater remediation. Journal of Industrial and Engineering Chemistry, v. 14:2, p. 145-156.

USEPA (1998) Permeable Reactive Barrier Technologies for Contaminant Remediation. EPA/600/R-98/125.

USEPA (2004) Evaluation of Permeable Reactive Barrier Performance. EPA 542-R-04-004.

Vogan, J.L.; Focht, R.M.; Clark, D.K. & Graham, S.L. (1999) Performance evaluation of a permeable reactive barrier for remediation of dissolved chlorinated solvents in groundwater. Journal of Hazardous Materials, v. 68:1-2, p. 97-108.

Wilkin, R.T. and McNeil, M.S. (2003) Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage. Chemosphere, v. 53:7, p. 715-725.