



# Nickel removal by zero valent iron/lapillus mixtures in column systems

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## Abstract

The remediation of contaminated groundwater, through permeable reactive barrier (PRB) technology, has raised strong interest in the field of environmental geotechnics. The use of granular mixtures composed of zero valent iron (ZVI) together with an inert and/or porous material is a new strategy for preventing the decrease in hydraulic conductivity of PRBs composed of pure ZVI alone.

In this paper, granular mixtures composed of ZVI and lapillus in different weight ratios were tested for nickel removal through column tests. The newly proposed material, lapillus, is a low-cost material (a by-product of pumice mining), readily available and efficient for nickel removal, as is shown by the benchmark column tests carried out in this paper. The weight ratio between ZVI and lapillus, the flow velocity and the initial contaminant concentration were the factors investigated in this paper since they can strongly influence the long-term removal efficiency and hydraulic behaviour of a PRB.

The column tests results were analysed in terms of hydraulic conductivity, nickel removal efficiency and the distribution of the removed nickel along the column over time. The test results clearly showed the great potential of the proposed ZVI/lapillus granular mixtures in terms of both removal efficiency and long-term hydraulic conductivity.

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**Keywords:** Permeable reactive barriers; Hydraulic conductivity; Groundwater; Remediation; Lapillus; Zero valent iron; Granular mixtures; Nickel

## 1. Introduction

Groundwater contamination is a widespread environmental problem in Italy and around the world. The study and application of different groundwater remediation technologies are themes frequently addressed in the field of environmental geotechnics. Among these technologies is the permeable reactive barrier (PRB) that represents a valid and sustainable *in situ* groundwater remediation technology. It consists of a diaphragm wall, filled with a reactive

medium and placed across the flow path of the contaminated groundwater, whose purpose is to retain the contaminants within the groundwater itself.

Zero-valent iron (ZVI) was firstly proposed as a reactive medium in PRBs to treat groundwater contaminated by halogenated organic solvents (Gillham and O'Hannesim, 1992). At a later stage, ZVI was used to treat many more contaminants (e.g., heavy metals, radionuclides and nitrates) mainly in PRBs, but also for stormwater and individual potabilization systems (Rangsivek and Jekel, 2005; Noubactep et al., 2010). It is estimated that 60% of the 200 PRBs installed worldwide are ZVI-based (Henderson and Demond, 2007; ITRC, 2011). The main issues related to the operational lifetime of ZVI systems are hydraulic conductivity preservation and contaminant removal efficiency in the long-term. In particular, the possible clogging

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of a PRB induces the bypass (development of preferential flow paths) of the system, by the contaminated plume, with the consequent loss in efficiency (Kamolpornwijit et al., 2003; Li and Zhang, 2007; Henderson, 2010; Jeen et al., 2011).

The causes of the decrease in hydraulic efficiency of ZVI systems lie in the expansive nature of iron corrosion (Caré et al., 2008; Zhao et al., 2011; Moraci et al., 2016); gas formation (Reardon, 1995, 2005, 2014; Henderson and Demond, 2011; Moraci et al., 2016); biofilm formation (Gu et al., 1999), the accumulation of secondary mineral precipitates (O'Hannesin and Gillham, 1998; Liang et al., 2000; Kamolpornwijit et al., 2003; Jeen et al., 2008) and, in the case of PRBs, the clogging of voids due to the movement of fine particles in the upstream soil into the PRB's pores (Moraci et al., 2013).

The main strategy developed to avoid the decrease in permeability with time in ZVI systems is to mix this medium with other granular materials, such as sand, pumice, gravel or anthracite (O'Hannesin and Gillham, 1998; Bi et al., 2009; Moraci and Calabrò, 2010; Moraci et al., 2011; Calabrò et al., 2012; Ruhl et al., 2012; Moraci et al., 2015a).

The groundwater quality is particularly affected by the presence of heavy metals (Panagos et al., 2013; Van Liedekerke et al., 2014) with nickel being among the heavy metals most difficult to remove (Moraci et al., 2013). Nickel is listed among the 33 Priority Substances, according to Annex II of the Directive on Environmental Quality Standards of the European Commission (Official Journal of the European Union, 2008), as required by the Water Framework Directive (Official Journal of the European Communities, 2000), and is among the 126 Priority Pollutants selected and prioritized by EPA in the Clean Water Act (P.L. 92-500, 1972), the Safe Drinking Water Act (P.L. 93-523, 1974), the Resource Conservation and Recovery Act (P.L. 94-580, 1976) and the Superfund Act (P.L. 96-510, 1980), which provides the protection of groundwater in the United States.

ZVI can remove heavy metals by a redox process, followed by cementation or precipitation, adsorption onto its corrosion products (i.e., adhesion of the contaminant to the surface of iron corrosion products) or co-precipitation (i.e., contaminants are incorporated into the matrix of the precipitating iron oxides) (Rangsviek and Jekel, 2005; Komnitsas et al., 2007; Cundy et al., 2008; Noubactep, 2008, 2009; Noubactep and Schöner, 2009; Moraci and Calabrò, 2010; Bilardi et al., 2013a; Bilardi et al., 2015). Since nickel has a standard electrode potential close to that of ZVI ( $E_{\text{Ni(II)/Ni(0)}}^0 = -0.25 \text{ V}$ ;  $E_{\text{Fe(II)/Fe(0)}}^0 = -0.44 \text{ V}$ ), a redox process is probably not quantitative so that the main mechanisms for nickel removal are co-precipitation with iron hydroxides, adsorption onto the (hydr)oxide surfaces, isomorphic substitution of Fe in the iron oxides structure or adsorptive size-exclusion (Herbert, 1996; Wang and Qin, 2007; Vodyanitskii, 2010; Bilardi et al., 2013b).

In order to improve the removal and hydraulic conductivity of a PRB, we propose here the use of natural volcanic lapillus as the admixing agent for ZVI instead of pure granular ZVI alone. Lapillus was chosen for its large availability and low cost, considering it is a by-product of pumice mining (Catalfamo et al., 2006). The granular mixtures between ZVI and lapillus were tested for nickel removal, and the effect of different parameters (i.e., weight ratio between ZVI and lapillus, flow velocity and contaminant initial concentration) on the long-term removal efficiency and hydraulic behaviour of ZVI/lapillus systems was investigated. Column tests using the pure materials, ZVI and lapillus, were also carried out and employed as benchmarks.

## 2. Materials and methods

### 2.1. Granular materials

The granular ZVI used in our experiments was type FERBLAST RI 850/3.5, distributed by Pometon S.P.A. (Mestre, Italy). The material mainly contained iron (>99.74%), although a small percentage of identified impurities included Mn (0.26%), O, S and C. The material was characterized by a uniform grain size distribution; the coefficient of uniformity  $U (d_{60}/d_{10})$  was 2. The mean grain size ( $d_{50}$ ) was approximately 0.5 mm. The particle density of the reactive material was  $7.87 \text{ g/cm}^3$ .

The granular lapillus was distributed by SEM "Società Estrattiva Monterosi" s.r.l., Viterbo, Italy. It mainly consisted of silica ( $\text{SiO}_2 = 47\%$ ) and oxides of various elements ( $\text{Al}_2\text{O}_3 = 15\%$ ,  $\text{K}_2\text{O} = 8\%$ ,  $\text{Na}_2\text{O} = 1\%$ ,  $\text{Fe}_2\text{O}_3\text{-FeO} = 7\text{-}8\%$ ,  $\text{MnO} = 0.15\%$ ,  $\text{MgO} = 5.5\%$  and  $\text{CaO} = 11\%$ ).

It was observed with Scanning Electron Microscopy (SEM) that the lapillus was characterized by an irregular and rough surface and non-homogeneous porosity (Fig. 1). Moreover, the shape of the lapillus particles appeared to be highly variable.

A gradation test using the wet method was carried out on the lapillus prior to the column tests in which the grains retained on sieve No. 20 (>0.84 mm) and those passing through sieve No. 200 (<0.074 mm) were discarded in order to obtain a particle size distribution as similar as possible to that of ZVI. The coefficient of uniformity  $U$  was 3.2 and the mean grain size ( $d_{50}$ ) was approximately 0.4 mm. The apparent particle density of the lapillus was  $2.2 \text{ g/cm}^3$ . The grain size distributions of the two granular materials are shown in Fig. 2.

The choice of grain size distribution for the reactive materials used in this research was based on filter criteria (Moraci, 2010; Moraci et al., 2012a, 2012b, 2013, 2015b). The grain size distributions of the chosen materials were uniform and corresponded to an internally stable filter.

### 2.2. Column tests

The column experiments were carried out using polymethyl methacrylate (PMMA—Plexiglas™) columns with

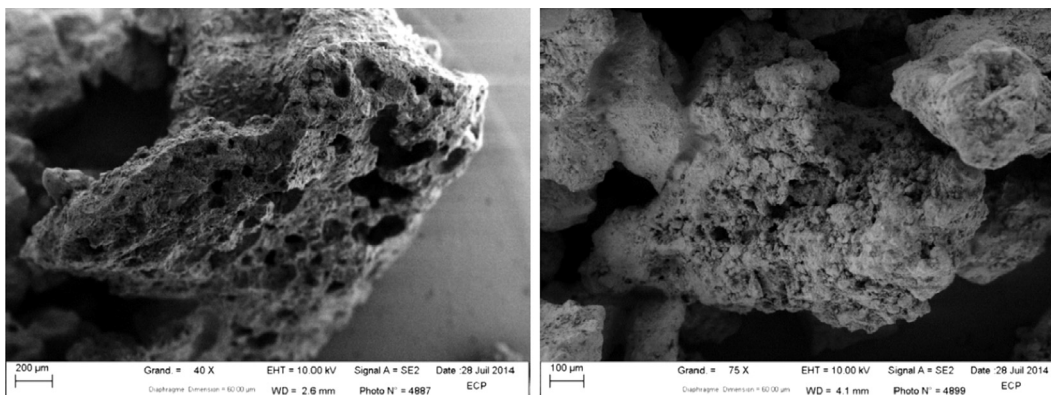


Fig. 1. SEM images of Lapillus samples using enlargements of 40× and 75×, respectively.

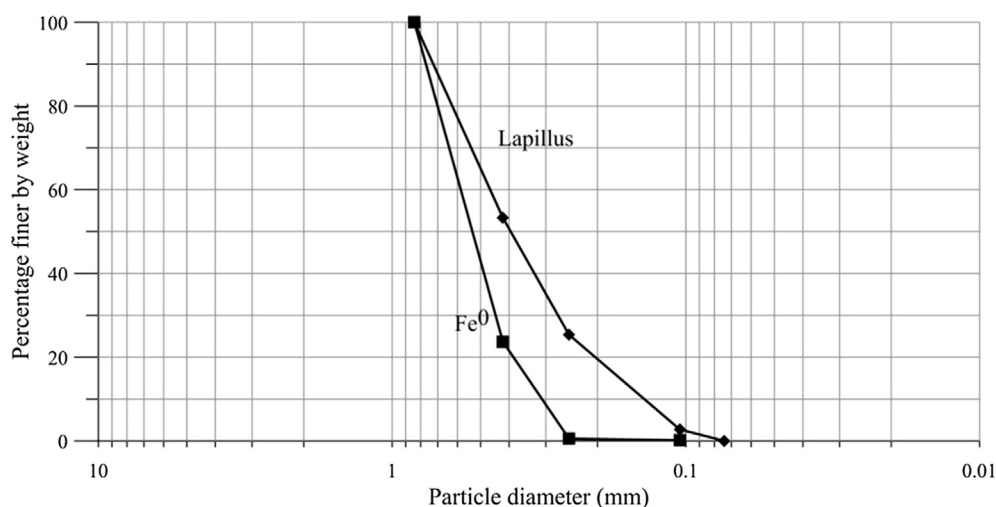


Fig. 2. Grain size distribution of ZVI and lapillus.

an internal diameter of  $5 \pm 0.1$  cm and a height of 50 cm, equipped with sampling ports located at different distances from the inlet (i.e., 3, 8, 18, 28, 38 and 50 cm). A portion of the reactive medium between two sampling ports was defined here as a “sector”. A peristaltic pump (Watson Marlow 205S) was used to feed the columns, under constant upward flow, from a single PE bottle. In all the tests, the flow velocity was kept constant over time. A schematic diagram of the column test apparatus is shown in Fig. 3.

Lapillus and ZVI were mixed at a prefixed weight ratio (w.r.) and the column was filled in layers in order to obtain a specimen as homogenous as possible. The reactive medium was flushed with the contaminated solution from the beginning of the test.

Three sets of experiments were carried out in order to study the influence of (i) the ZVI/lapillus weight ratio, (ii) the flow velocity and (iii) the initial contaminant concentration on the long-term nickel removal efficiency and the hydraulic behaviour of the ZVI/lapillus mixtures (Table 1).

The first set of column tests was performed using three different ZVI/lapillus w. r. (10:90, 30:70 and 50:50, respectively), a nickel solution with an initial concentration of

50 mg/L and a constant Darcy velocity equal to 0.4 m/d (flow rate equal to 0.5 mL/min).

The second set of column tests was carried out using a constant granular mixture characterized by w.r. 30:70, a nickel solution with an initial concentration of 50 mg/L, as before, and three different flow velocities corresponding to 0.079 (flow rate equal to 0.1 mL/min), 0.4 (flow rate equal to 0.5 mL/min) and 1.9 m/d (flow rate equal to 2.5 mL/min), respectively.

The third and final set of experiments was performed using a constant granular mixture characterized by w.r. 30:70, solutions at three different initial nickel concentrations (10, 50 and 100 mg/L, respectively) and a constant flow velocity equal to 0.4 m/d (flow rate equal to 0.5 mL/min).

Two benchmark tests using pure ZVI (Moraci and Calabrò, 2010) and pure lapillus, respectively, were also considered.

The contaminated aqueous solutions were prepared by dissolving nickel (II) nitrate hexahydrate (purity 99.999, Sigma-Aldrich, Germany) in distilled water. The pH and Eh values were directly measured on the samples (Inolab

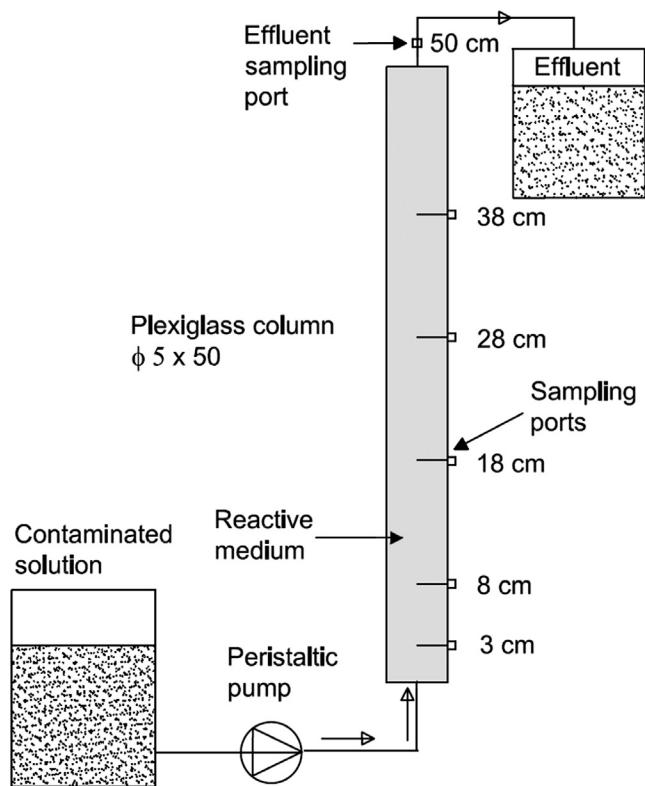


Fig. 3. Schematic diagram of column test apparatus.

pH/Cond 720). Furthermore, the aqueous concentrations of nickel in the samples, collected during the column tests, were measured using ICP-OES (Perkin Elmer OPTIMA 8000), according to conventional Standard Methods (APHA, 2005). The spectrophotometer was calibrated, before each set of analyses, using three operational standard solutions covering the expected range in concentration of the samples (from a minimum value of 0.01 mg/L to a maximum value of 5 mg/L), following dilution. Each operational standard solution was prepared by an appropriate dilution of 1000 ppm of a certified multi-element standard. The minimum correlation coefficient of the calibration curves was of 0.997. During the column tests, performed at room temperature ( $20 \pm 4$  °C), the hydraulic conductivity was determined by the falling-head

( $k < 10^{-6}$  m/s) or constant-head ( $k > 10^{-6}$  m/s) permeability method (Head and Keeton, 2008).

### 3. Results and discussion

#### 3.1. Benchmark column test results

The column test performed with the pure granular lapillus demonstrated the capacity of this volcanic material to reduce the nickel concentration to a certain extent. The experimental results were plotted in terms of the normalized nickel concentration ( $C/C_0$ ) and the pH as a function of time (h) at the outlet (Fig. 4a) and in terms of different sampling times (from 120 to 1248 h) as a function of the column length (Fig. 4b). From the beginning of the experiment until about 500 h, the pH at the outlet remained constant and was around 7, but the pH went down to 6 after 500 h (pH of the influent solution was about 6.5) and, at the same time, a breakthrough occurred (that is typically defined as the point where a rapid increase in concentration in the effluent of a substance is clear; see also Fig. 4a).

The hydraulic conductivity was almost constant (around  $2.5 \times 10^{-4}$  m/s) during the whole duration of the test.

The removal efficiency ( $Eff$ ) was calculated according to Eq. (1):

$$Eff[\%] = M_{Nickel\_rem} / M_{Nickel\_in} \quad (1)$$

where  $M_{Nickel\_rem}$  is the mass of removed nickel, calculated using a mass balance, and  $M_{Nickel\_in}$  is the mass of nickel at input.

The specific removed mass ( $M_{sr}$ ) was calculated according to Eq. (2):

$$M_{sr}[\text{mg/g}] = M_{Nickel\_rem} / M_{rm} \quad (2)$$

where  $M_{rm}$  is the mass of reactive medium contained in the column.

The efficiency and specific mass removed at 200 h were 99% and 0.14 mg<sub>Ni</sub>/g<sub>lapillus</sub>, respectively, and at breakthrough were 98% and 0.5 mg<sub>Ni</sub>/g<sub>lapillus</sub>, respectively, after 18 days. The efficiency decreased to 35% after 1000 h.

Therefore, the column test results demonstrated that the lapillus was not completely inert towards the nickel removal, but showed a removal capacity probably related

Table 1  
Column test program.

ID	Reactive medium	Mass of lapillus [g]	Mass of ZVI [g]	Initial nickel concentration [mg/L]	Flow velocity [m/d]	Porosity [%]	Residence time [h]	Input mass [mg]	Test duration [days]
1	ZVI <sup>a</sup>	–	240	50	0.4	44	0.70	2540	70
2	Lapillus	1289	–	50	0.4	35	15.07	1872	52
3	Mix ZVI/lapillus 10:90	1242	138	50	0.4	36	15.03	7776	216
4	Mix ZVI/lapillus 30:70	1120	480	50	0.4	37	15.01	9000	250
5	Mix ZVI/lapillus 50:50	970	970	50	0.4	38	14.69	7992	222
6	Mix ZVI/lapillus 30:70	1106	474	10	0.4	38	15.20	3614	>502 <sup>b</sup>
7	Mix ZVI/lapillus 30:70	1113	477	100	0.4	37	15.10	8655	120
8	Mix ZVI/lapillus 30:70	1104	473	50	0.079	37	74.64	7646	>1062 <sup>b</sup>
9	Mix ZVI/lapillus 30:70	1093	468	50	1.9	38	3.08	6442	35

<sup>a</sup> 3 cm reactive zone length (Moraci and Calabrò, 2010).

<sup>b</sup> Tests still in progress.



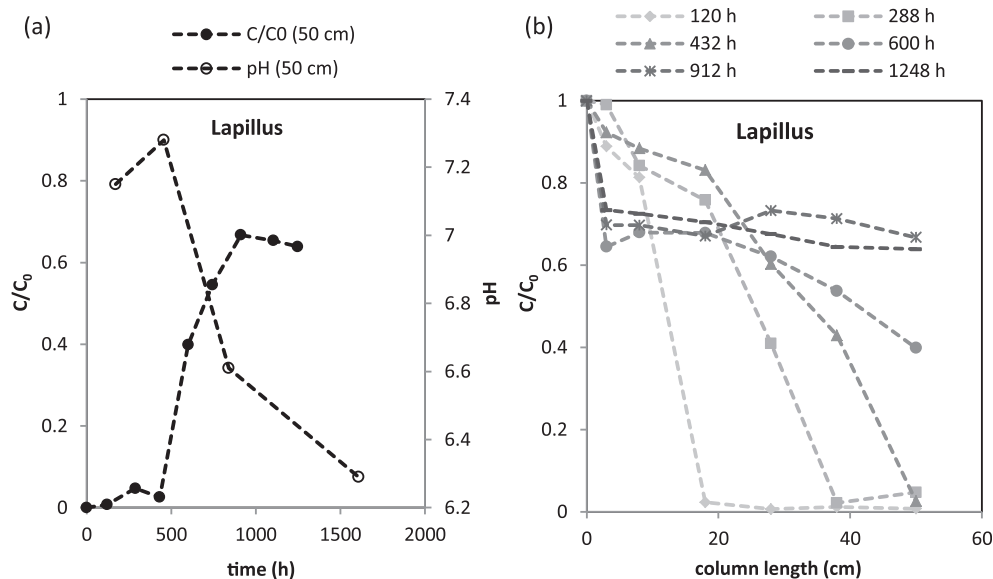


Fig. 4. (a) Normalized nickel concentration ( $C/C_0$ ) and pH as functions of time (h) at outlet and (b) normalized nickel concentration ( $C/C_0$ ) as function of column length (cm).

to its chemical composition (presence of metal oxides) and to the high specific surface (due to surface roughness), which influenced the adsorption process.

Previous authors (Moraci and Calabrò, 2010) put the pure granular ZVI column (exposed to the same setup and materials, mass of 240 g, corresponding to a height of the reactive zone of 3 cm) in contact with the same nickel-contaminated solution. They found that the efficiency and specific mass removed after 200 h were 49% and 0.73  $\text{mg}_{\text{Ni}}/\text{g}_{\text{ZVI}}$ , respectively. The limited nickel removal capacity of the 3 cm ZVI layer was attributed to the insufficient residence time.

### 3.2. Influence of ZVI/lapillus weight ratio

Column tests with mixtures of ZVI and lapillus at different w.r. (i.e., 10:90, 30:70 and 50:50) were performed to verify the influence of this parameter on the mixture removal efficiency. The tests were carried out under the same experimental conditions of flow velocity (0.4 m/d) and initial nickel concentration ( $C_0 = 50 \text{ mg/L}$ ).

Fig. 5 shows the variations in normalized nickel concentration and pH as functions of time for each granular mixture. The removal efficiency of nickel by the reactive medium was clearly linked to the amount of ZVI used, the least efficient mixture being the 10:90 w.r. (Fig. 5a) and the most efficient being the 50:50 w.r. (Fig. 5c).

As expected, and in line with previously published results, the pH value increased from the initial value (pH of the influent solution was about 6.5) due to iron corrosion, which consumed  $\text{H}^+$  (Bilardi et al., 2013b). As previously demonstrated, a pH value higher than 5 suggests that nickel can be removed from the aqueous phase by adsorption, co-precipitation and adsorptive size exclusion (Noubactep, 2008, 2009). Thus, the removal efficiency is

higher when the pH is alkaline or neutral and the Eh, on the contrary, presents negative values. In the present experiments, the measured concentration of nickel increased and a nickel breakthrough occurred as the pH decreased and the Eh increased (Fig. 5). Therefore, the extent of the contaminant removal seems to depend on the kinetics of iron corrosion (Bilardi et al., 2013b).

The results of the column tests in terms of nickel removal efficiency (Eq. (1)) and the specific mass removed at the breakthrough (Eq. (2)) are shown in Table 2. As the table suggests, 6, 3 and 1.5 g of nickel flowed into the columns and were retained by the mixtures at w.r 50:50, 30:70 and 10:90, respectively, with a removal efficiency greater than 99%. The specific mass removed  $M_{sr}$  at the breakthrough expressed the removal capacity (RC) of the three reactive media, which is a design parameter for the determination of the barrier thickness ( $L$ ) that can be calculated according to Eq. (3) (Moraci et al., 2015a):

$$L = \frac{M_{\text{contaminant}}}{RC \cdot H \cdot W \cdot \gamma_{rm}} \quad (3)$$

where  $M_{\text{contaminant}}$  is the mass of the contaminant to be removed,  $H$  and  $W$  are the depth and width of the barrier, respectively, and  $\gamma_{rm}$  is the unit weight of the reactive medium.

Another method for determining the thickness of a hypothetical PRB is to analyze the nickel concentration data through a first order kinetic model (Bilardi et al., 2016).

In order to evaluate the influence of w.r., the cumulated mass of removed nickel was depicted (Fig. 6) as a function of the nickel mass in input and at the time of each test, considering the same reactive medium thickness (i.e., 3 cm, 18 cm and 50 cm from the column inlet). When a thickness of 3 cm from the column inlet was considered, the 50:50 w.r.

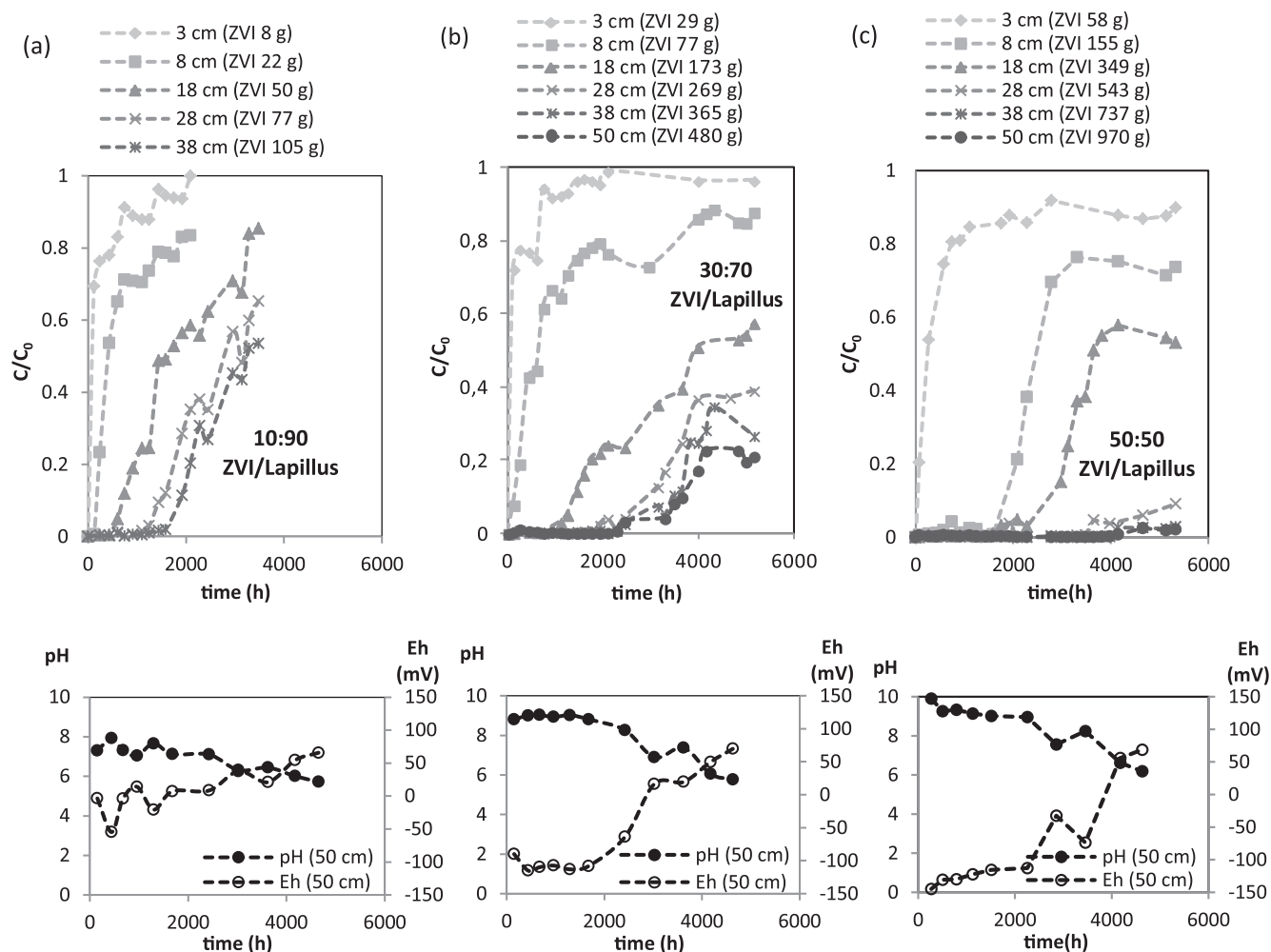


Fig. 5. Normalized nickel concentration ( $C/C_0$ ) for different sampling ports and pH and Eh at outlet as functions of time (h) for (a) 10:90, (b) 30:70 and (c) 50:50 ZVI/lapillus w.r. mixtures.

Table 2  
Column test results: influence of weight ratio.

Weight ratio	Breakthrough time at outlet [d]	$M_{sr}$ at breakthrough [ $\text{mg}_{\text{Ni}}/\text{g}_{\text{mix}}$ ]	Removal efficiency [%]		
			1000 [h] – 1.5 [ $\text{g}_{\text{Ni}}$ ]	2000 [h] – 3 [ $\text{g}_{\text{Ni}}$ ]	4000 [h] – 6 [ $\text{g}_{\text{Ni}}$ ]
10:90	66 (105 PV)	1.7	99.6	97.6	83.2
30:70	102 (163 PV)	2.3	99.4	99.6	94.4
50:50	194 (316 PV)	5.6	99.7	99.7	99.8

granular mixture showed an efficiency greater than the 3 cm ZVI alone (Fig. 6a), despite the lower ZVI content, due to the contribution of lapillus in terms of the nickel removal.

When a thickness of 18 cm from the column inlet was considered, the removal efficiency decreased more quickly due to the lower ZVI content in the mixture (Fig. 6b).

Finally, for a thickness of 50 cm of the reactive medium, the removal efficiency after about 1200 h from the beginning of the test (1800 mg of nickel mass in input) was about 99.9% for all three granular mixtures, while it was equal to

65% and 30% for the tests performed using pure granular lapillus and ZVI, respectively (Fig. 6c). Therefore, the mixtures behaved better than the pure granular media (i.e., lapillus and ZVI). In fact, when a high concentration of nickel was considered (i.e., 50 mg/l), the reactivity of the pure lapillus was limited in time, as opposed to when lapillus was in the presence of ZVI, which brought about a significant increase in reactivity.

An additional comparison among the three granular mixtures was carried out considering the same ZVI mass. As shown in Fig. 7, the cumulated mass of removed nickel

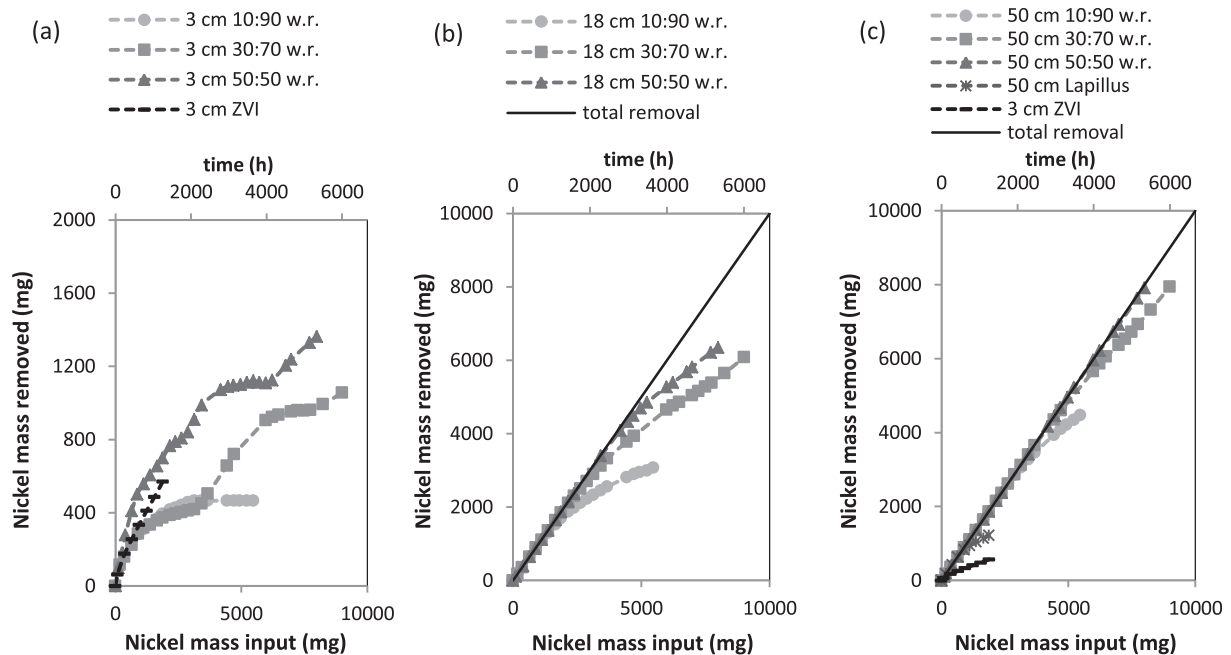


Fig. 6. Nickel mass removed (mg) as function of nickel mass in input (mg) and at time (h) considering (a) 3 cm, (b) 18 cm from inlet and (c) at outlet for three ZVI/lapillus mixtures and benchmark column tests.

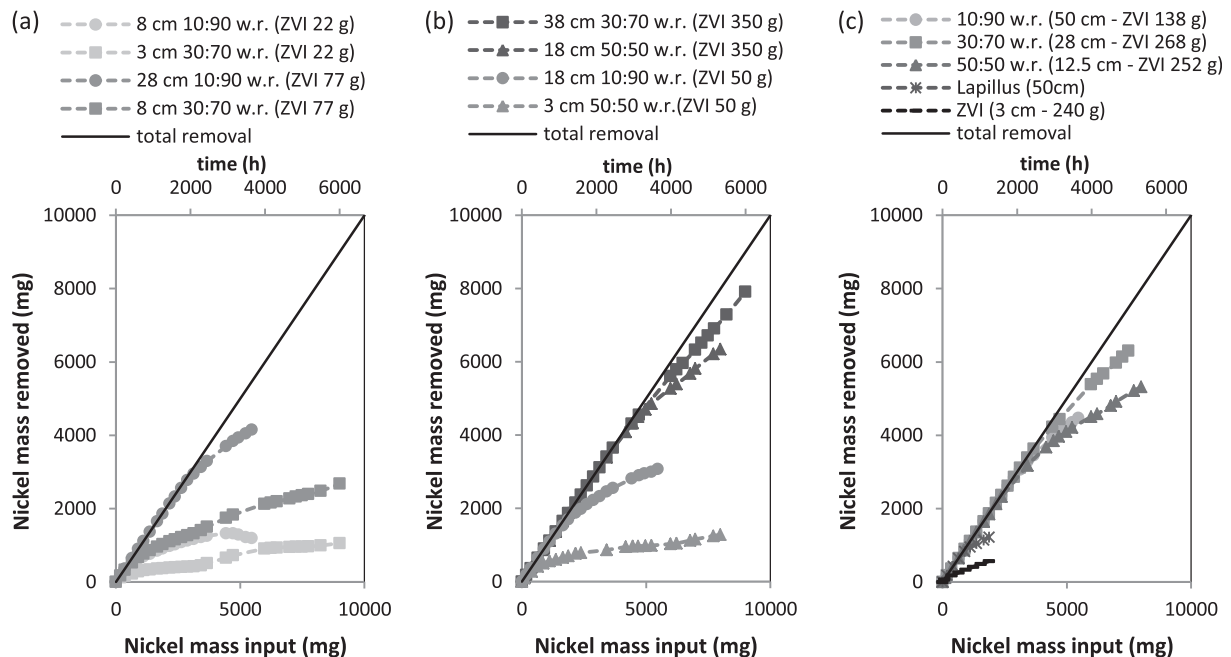


Fig. 7. Nickel mass removed (mg) as function of nickel mass in input (mg) and of time (h) for (a) ZVI masses of about 22 and 77 g, (b) ZVI masses of about 50 and 350 g and (c) different reactive medium thicknesses.

was plotted as a function of the nickel mass in input and of time considering the same ZVI mass for the three different granular mixtures (corresponding to different reactive medium thicknesses). In each comparison, the best behaviour was observed for the column with the w.r. containing the lowest percentage of ZVI, which demonstrates the ability of lapillus to optimize the use of ZVI by increasing the res-

idence time that is beneficial for Ni removal, as previously demonstrated for other granular mixtures (Moraci and Calabrò, 2010; Calabrò et al., 2012; Moraci et al., 2015a).

In Fig. 7c, in particular, it is interesting to note that the 10:90 mixture (thickness equal to 50 cm and ZVI mass of 138 g) was more efficient than the 50:50 granular mixture (thickness of 12.5 cm and ZVI mass of 252 g). Therefore,

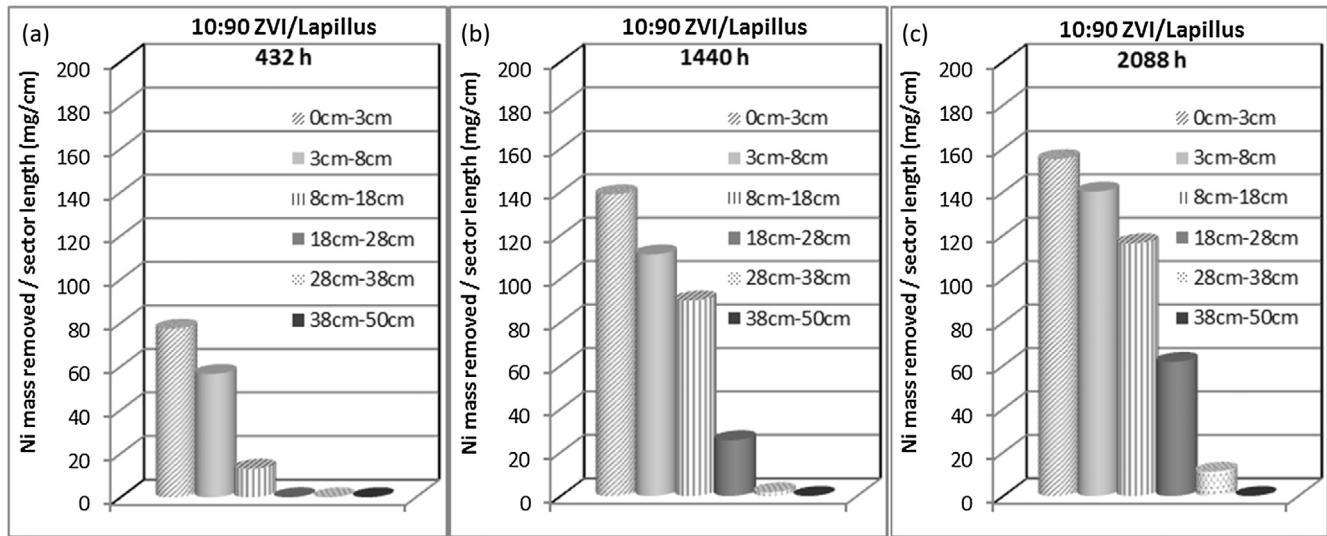


Fig. 8. Nickel mass removed in each sector divided by length of sector for 10:90 ZVI/lapillus w.r. mixture at (a) 432, (b) 1440 and (c) 2088 h.

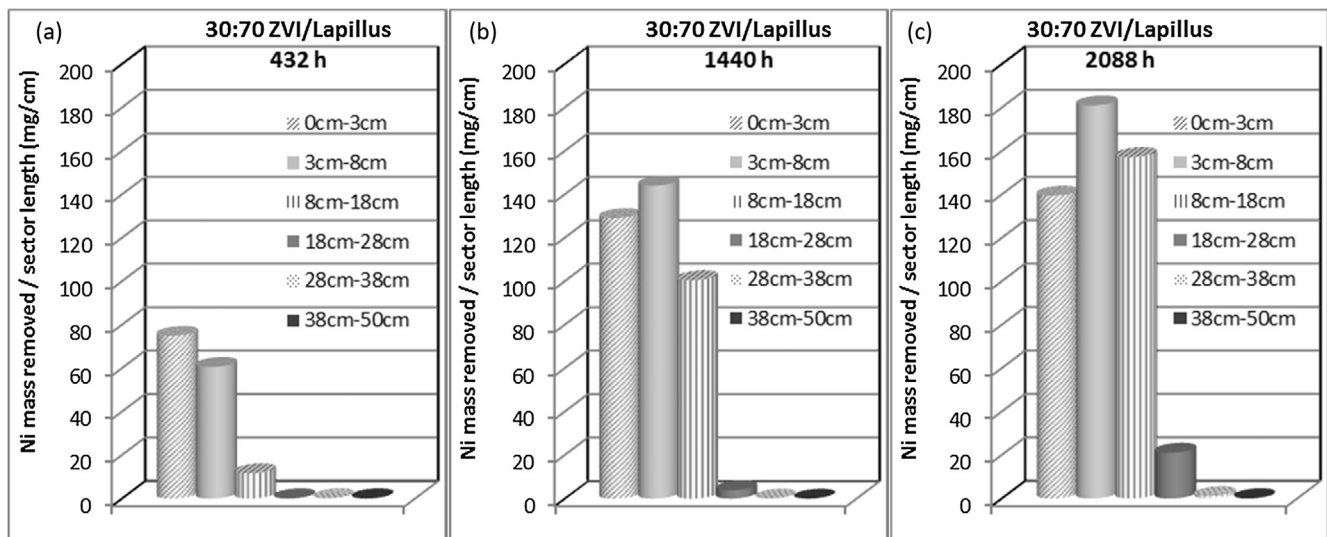


Fig. 9. Nickel mass removed in each sector divided by length of sector for 30:70 ZVI/lapillus w.r. mixture at (a) 432, (b) 1440 and (c) 2088 h.

the results of the present tests show that the residence time and the lapillus mass appear to be crucial in nickel removal.

In order to understand which sector of the column was most affected by the nickel mass removal, which is also a clue to understanding which sector was most critical in the case of a possible loss in permeability, the cumulated mass of removed nickel (derived by a mass balance) in each sector, divided by the length of the sector considered, was reported following 432, 1440 and 2088 h from the beginning of the test for the 10:90, 30:70 and 50:50 ZVI/lapillus w.r. mixtures (Figs. 8–10). As can be seen from the results in the graphs, the nickel mass removal was observed to be almost homogeneous in the first 18 cm of the column sector for the 10:90 and 30:70 granular mixtures, while the nickel mass removal was mainly concentrated in the first 8 cm for

the 50:50 granular mixture due to the higher amount of ZVI present. In fact, the mass of removed nickel was significantly higher near the inlet (Figs. 8 and 9). This behaviour can be explained by the fact that most probably the ZVI present in the column downstream to a thickness equal to about 18 cm was consumed by the reactions with water and other compounds that were possibly present (e.g., nitrates), also in absence of the contaminant that was removed upstream.

Fig. 11 reports the same data for the 30:70 and 50:50 ZVI/lapillus mixtures after about 5400 h.

The trends over time of the hydraulic conductivity for the three ZVI/Lapillus mixtures are shown in Fig. 12. A slight increase in hydraulic conductivity is observed at the beginning of the tests, probably due to an increase in saturation with time.



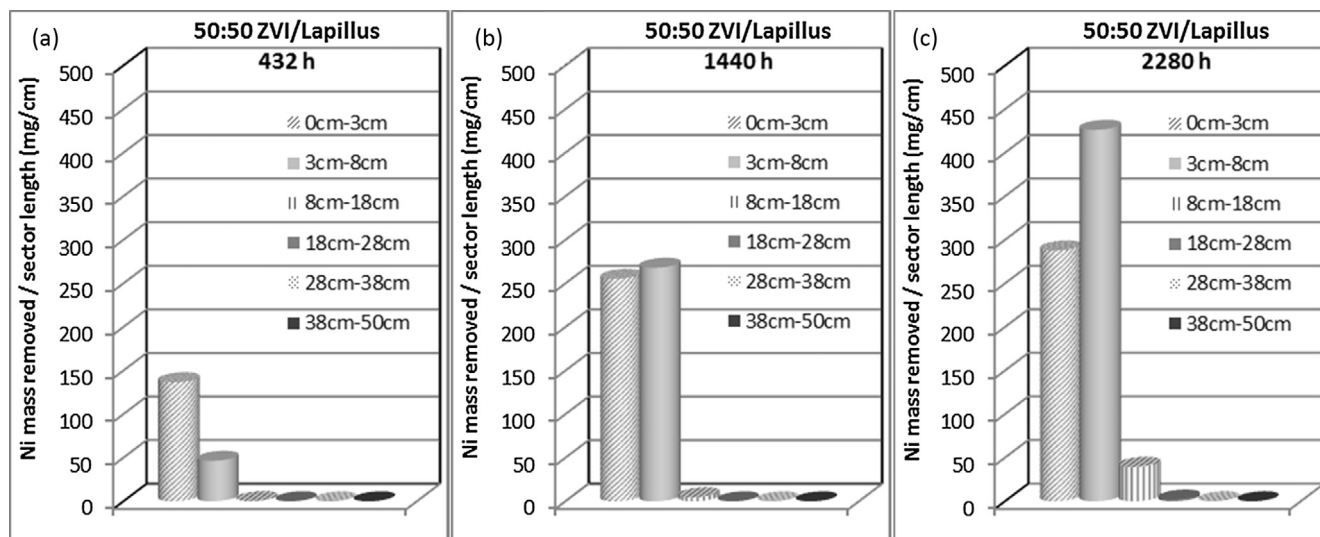


Fig. 10. Nickel mass removed in each sector divided by length of sector for 50:50 ZVI/lapillus w.r mixture at (a) 432, (b) 1440 and (c) 2280 h.

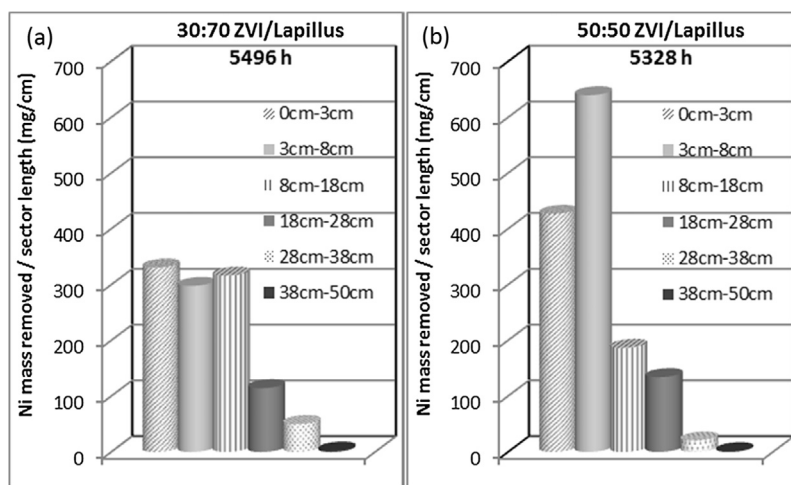


Fig. 11. Nickel mass removed in each sector divided by length of sector for (a) 30:70 ZVI/lapillus w.r. mixture at 5496 h and (b) 50:50 ZVI/lapillus w.r. mixture at 5328 h.

The highest reduction in hydraulic conductivity, corresponding to about two orders of magnitude compared to the initial value, was observed for the 50:50 mixture, while the best hydraulic behaviour was observed for the 10:90 mixture, which should guarantee a slightly higher permeability over the long term than the 30:70 mixture.

It is known that the hydraulic conductivity of ZVI systems can decrease because of mineral precipitation, gas formation or the expansive nature of iron corrosion products (and particle clogging that can be disregarded if the filter is designed respecting the conditions for the internal stability of granular materials). In our experimental system, where the ZVI particles were more dispersed (per unit volume), thanks to the admixing agent, the fraction of voids involved in the aforementioned phenomena, all strictly linked to the presence of iron, was lower and the medium less subject to clogging.

Thus, the reduction in hydraulic conductivity observed in our experimental conditions, for the 50:50 mixture, was linked to the higher ZVI content per unit volume of the column, and consequently, to the higher quantity of corrosion products and gases. These results can also be obtained using theoretical numerical models similar to those previously developed by the authors (Moraci et al., 2016).

### 3.3. Influence of flow velocity

Three column tests were carried out by varying the flow velocity (i.e.,  $v_1 = 0.079$  m/d,  $v_2 = 0.4$  m/d and  $v_3 = 1.9$  m/d) in order to study the influence of this parameter on the long-term nickel removal efficiency and hydraulic behaviour of a 30:70 w.r. ZVI/lapillus granular mixture. All

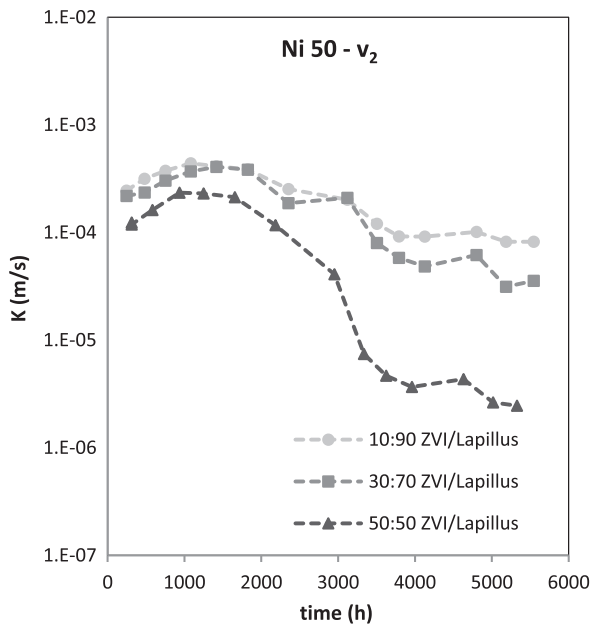


Fig. 12. Hydraulic conductivity profile (m/s) as function of time (h).

the tests were performed using a solution of nickel at an initial concentration of 50 mg/L (Table 1).

Fig. 13a shows the variation in the normalized nickel concentration as a function of time for two different sampling ports (28 and 50 cm from the column inlet) and relative to each of the three values of flow velocity used.

The best behaviour in terms of nickel removal was observed for the column test performed at flow velocity  $v_1$  (test still in progress). More specifically, in this column test, the breakthrough was observed at 28 cm and after about 750 days (Fig. 13a), while at the outlet, the system was still fully efficient after 862 days (test still in progress). In contrast, in the column test performed at flow velocity

$v_3$ , the reactive medium showed a rapid exhaustion and the breakthrough was observed at 28 cm and at the outlet after only 2.6 and 3.8 days, respectively (Fig. 13a). Finally, the column test performed at flow velocity  $v_2$  presented an intermediate behaviour between the two and the breakthrough was observed at 28 cm and at the outlet after 80 and 102 days, respectively (Fig. 13a).

The present results clearly suggest that an increase in flow velocity leads to a decrease in removal efficiency of the reactive medium, highlighting the non-linearity of the removal and confirming the importance of guaranteeing a residence time sufficient for the complete removal of the contaminant. Similar results were also found by the authors for ZVI/pumice mixtures (Moraci et al., 2015a).

To investigate whether the slower exhaustion of the reactive medium observed above corresponded to a higher removal efficiency, we compared the three tests, as described above, with the same contaminant mass in input. Thus, the cumulated mass of removed nickel was plotted as a function of the cumulated mass of nickel in input for the three column tests (Fig. 13b). The graph confirms the behaviour observed in terms of the normalized nickel concentration. The removed mass of nickel for the same mass of reactive medium and for the same mass of nickel input varied with the flow velocity. Before exhaustion, for a reactive medium 50 cm in thickness, the masses of removed nickel were 4400 and 1400 mg for the tests performed at flow velocities  $v_2$  and  $v_3$ , respectively. Interestingly, the exhaustion has not been reached to date (>862 days) for the column test carried out with the lowest velocity.

The distribution in a 30:70 w.r. ZVI/lapillus granular mixture of mass of removed nickel per unit of column length, for each column sector (0–3 cm, 3–8 cm, 8–18 cm, 18–28 cm, 28–38 cm and 38–50 cm) and for the three column tests carried out at flow velocities  $v_1$ ,  $v_2$  and  $v_3$ , is

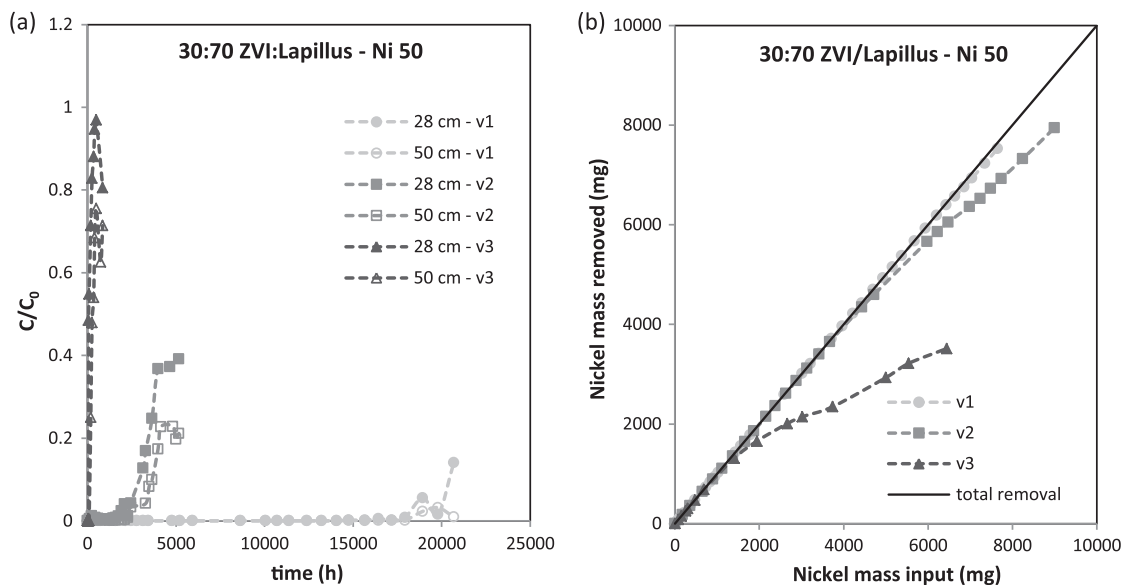


Fig. 13. (a) Normalized nickel concentration ( $C/C_0$ ) as function of time (h) at 28 and 50 cm from column inlet and (b) Nickel mass removed (mg) as function of nickel mass in input (mg) for column tests carried out at  $v_1$ ,  $v_2$  and  $v_3$  flow velocities.

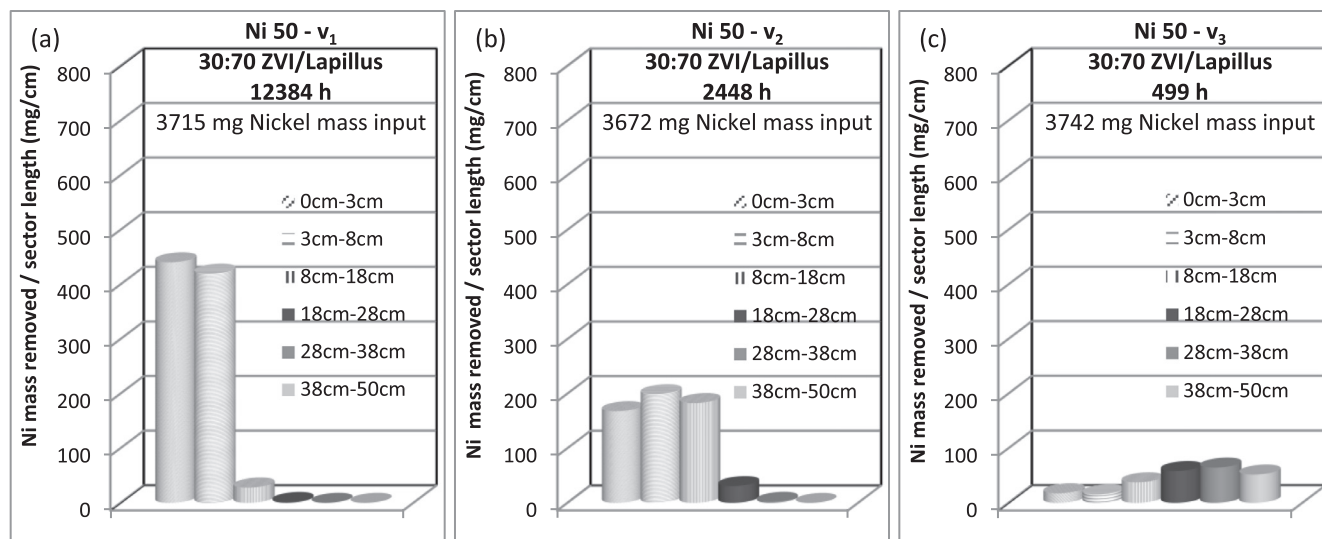


Fig. 14. Nickel mass removed in each sector divided by length of sector for column tests carried out at (a)  $v_1$ , (b)  $v_2$  and (c)  $v_3$  flow velocities.

Table 3  
Column test results: influence of flow velocity.

$v$ [m/d]	Breakthrough time at outlet [d]	$M_{sr}$ at breakthrough [ $\text{mg}_{\text{Ni}}/\text{g}_{\text{mix}}$ ]	Removal efficiency [%]			
			Mass of nickel in input			
			1000 mg	2000 mg	4000 mg	6000 mg
$v_1 = 0.079$	789 (253 PV)	3.6	99.9	99.9	99.9	99.8
$v_2 = 0.4$	102 (163 PV)	2.3	99.3	99.5	98.8	88.3
$v_3 = 1.9$	8 (60 PV)	0.84	97	85.2	62.8	56.3

shown in Fig. 14. The mass of removed nickel was equally distributed in the first 8 and 18 cm of the reactive medium thickness at flow velocities  $v_1$  and  $v_2$ . The entire thickness of the reactive medium was involved in the nickel removal in the test carried out using the highest value of flow velocity ( $v_3$ ). In particular, in this last case, the mass of removed nickel was more concentrated between the sampling port located at 18 cm from the column inlet and the outlet. Once again, it is clear that the specific removal efficiency was higher at the lowest flow velocity.

Hydraulic conductivity values did not highlight significant variations among the three reactive media. In particular, it remained constant with an average value of about  $3.8 \times 10^{-4}$  m/s and  $5.2 \times 10^{-4}$  m/s for the column tests carried out with the highest and lowest values of flow velocity, respectively.

Table 3 summarizes the specific mass of removed nickel and the removal efficiency calculated at the outlet for the four values of nickel mass input and for each column test.

#### 3.4. Influence of initial contaminant concentration

Three column tests were performed to study the influence of the initial contaminant concentration on the long-term nickel removal efficiency and hydraulic behaviour. For this purpose, the tests were conducted with a constant 30:70 ZVI:lapillus granular mixture at a flow velocity of 0.4

m/d and using solutions characterized by three different initial nickel concentrations (10, 50 and 100 mg/L, respectively). The characteristics of the column tests are reported in Table 1.

Fig. 15a shows the variation in normalized nickel concentration as a function of time for two different sampling ports (18 and 50 cm from the column inlet) and for each contaminated solution.

Considering the test carried out using the 10 mg/L solution (Fig. 15a), a breakthrough has not been observed yet at the sampling port located 18 cm from the inlet after 502 days (test still in progress). Considering the test carried out using the 100 mg/L solution, a thickness of 50 cm of reactive medium was able to efficiently reduce the nickel concentration for only 100 h (Fig. 15a). In the test performed using the 50 mg/L solution, a breakthrough occurred at around 37.5 and 83.3 days at 18 cm from the column inlet and at the outlet, respectively (Fig. 15a).

In Fig. 15b, the cumulated mass of removed nickel at the outlet is shown as a function of the nickel mass in input. As can be observed, the removal efficiency of the reactive medium decreased with an increase in the initial nickel concentration. Nickel was always efficiently removed at an initial concentration of 10 mg/L. The removal efficiency dropped down to 50% when the reactive medium (8000 mg of nickel mass in input) was permeated by a solution containing 100

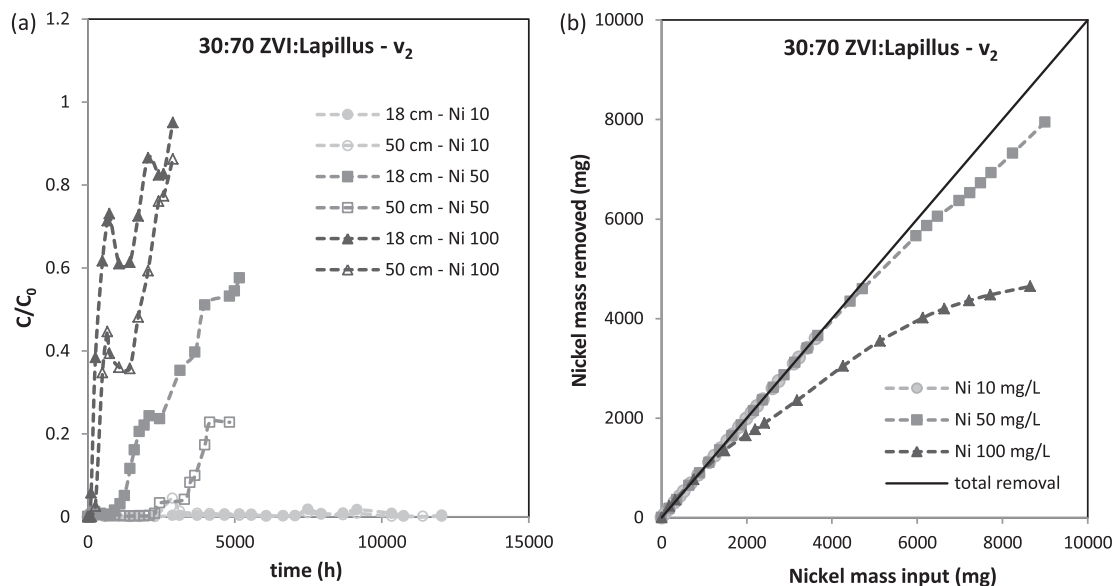


Fig. 15. (a) Normalized nickel concentration ( $C/C_0$ ) as function of time (h) for two different sampling ports (18 and 50 cm from column inlet) and (b) Nickel mass removed (mg) as function of contaminant mass in input (mg) for three contaminated solutions.

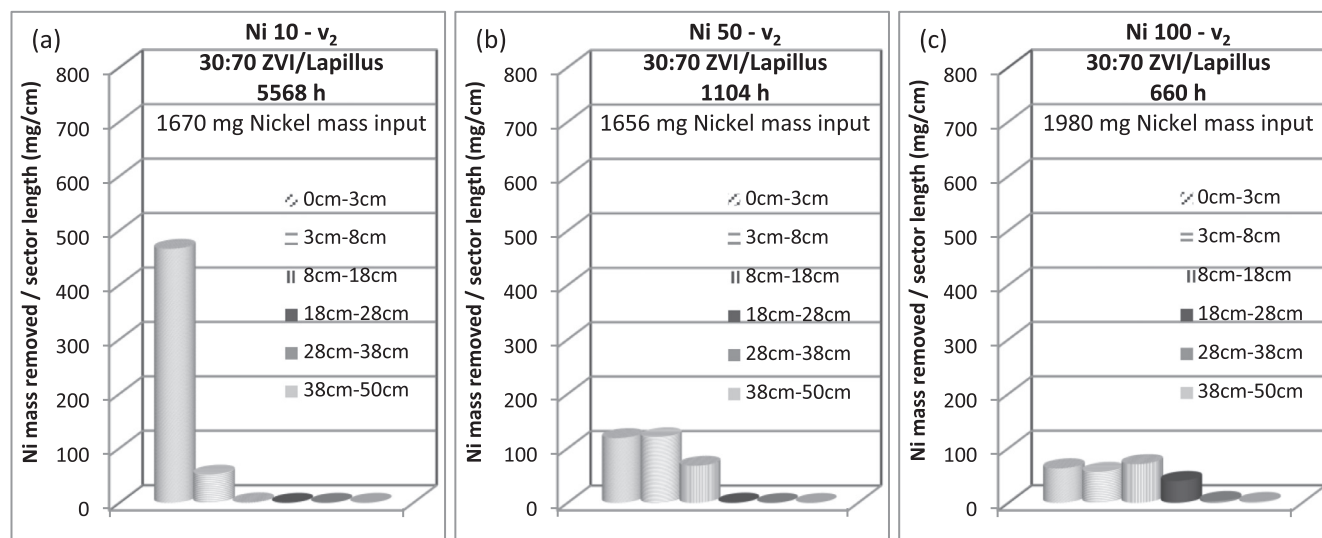


Fig. 16. Nickel mass removed in each sector divided by length of sector for column tests carried out using solutions at (a) 10, (b) 50 and (c) 100 mg/L of initial nickel concentration.

mg/L of initial nickel concentration and to 88% when the reactive medium (9000 mg of nickel mass in input) was permeated by a solution containing 50 mg/L of initial nickel concentration. The distribution of the mass of removed nickel (calculated through a mass balance) in each sector of the column test for the aforementioned three initial nickel concentrations, and at approximately the same nickel mass in input, is depicted in Fig. 16. The nickel mass was mainly removed in the first 3, 18 and 28 cm of the reactive medium in the tests carried out using the solutions at 10 (Fig. 16a), 50 (Fig. 16b) and 100 (Fig. 16c) mg/L of initial nickel concentration, respectively.

Our experimental conditions have confirmed that a lower mass flow of contaminant allows for the full exploitation of the reactive medium.

In Fig. 17a, the values for the removed mass of nickel per unit length (mg/cm) in the first sector (0–3 cm) of the column as a function of the initial contaminant concentration are reported for a preset value of mass of contaminant at input (the same as that considered in the above analysis).

It is observed that the points representing the experimental values can be described using an equation with a negative exponent.

Finally, the hydraulic conductivity as a function of the nickel mass input is depicted in Fig. 17b. The column showing the best hydraulic behaviour was that permeated with the highest value of initial nickel concentration (i.e., 100 mg/l). In contrast, a decrease in hydraulic conductivity of about three orders of magnitude was observed for the column test performed with the solution at 10 mg/L. This



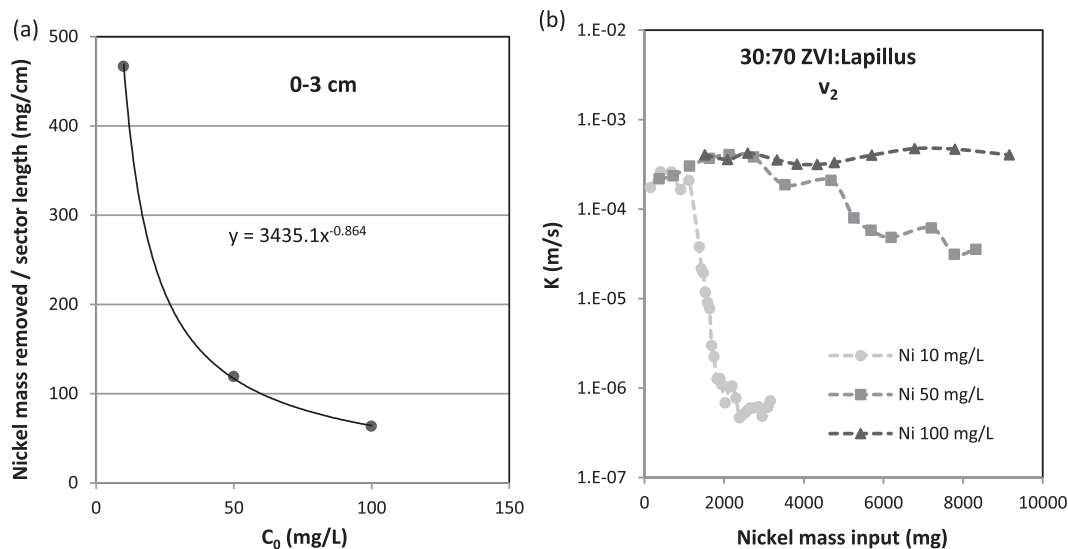


Fig. 17. (a) Nickel mass removed per unit length in first sector (0–3 cm) of column as function of initial contaminant concentration and (b) hydraulic conductivity (m/s) as function of nickel mass in input (mg).

phenomenon can probably be linked to the mass of removed nickel that was concentrated in the first 3 cm of the reactive medium (Fig. 16a). The final value for the hydraulic conductivity observed in this test corresponded to that of a fine sand. For the design of PRBs, the compatibility of the hydraulic conductivity of the barrier with that of the base soil must be assured in order to meet the permeability criterion of granular filters.

In this respect, as demonstrated by Moraci et al. (2015a) for ZVI/pumice mixtures, a mixture with a lower ZVI content appears to be more appropriate when the contaminated water is more diluted.

#### 4. Conclusions

Based on an analysis of the column tests, the following conclusions can be drawn:

- Lapillus is a suitable admixing agent for ZVI since it allows for both the optimization of the use of ZVI and the preservation of its hydraulic conductivity.
- The choices of the more appropriate ZVI/lapillus weight ratio and the barrier thickness depend on the contaminant mass to be removed. In particular, a comparison among three possible granular mixture weight ratios has shown the influence of the residence time and the lapillus mass, which appear to be more important variables than the amount of ZVI mass itself.
- The removal efficiency is not proportional to the ZVI content of the mixture. In particular, it has been observed that while the reactive zone for nickel removal proceeds from the inlet to the outlet of the column, the removal efficiency does not remain constant. It can be hypothesized that the ZVI present in the part of the column initially of interest to the contaminated plume, is

further consumed in the reactions with water and with other constituents possibly present (e.g., nitrates), decreasing its removal capacity.

- Flow velocity greatly influences the removal efficiency; in fact, the higher the flow velocity, the lower the residence time and the removal efficiency shown by the reactive medium.
- The removal efficiency of the reactive medium decreases as the contaminant concentration input increases.
- The distribution of the mass of removed nickel is linked to all the different parameters considered in this study (mixture weight ratio, flow velocity and nickel concentration) and is not always homogenous along the column length, which significantly influences the hydraulic conductivity.
- Based on the results of this study, the design parameters (i.e., filter width, ZVI/lapillus weight ratio and total mass of ZVI) must be adjusted according to the expected flow velocity and the concentration of contaminants in the water to be treated on the basis of column tests carried out under conditions that should be as similar as possible to those *in situ*.

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