



Estimate of the optimum weight ratio in Zero-Valent Iron/Pumice granular mixtures used in permeable reactive barriers for the remediation of nickel contaminated groundwater

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ARTICLE INFO

Article history:

Received 14 December 2010
Received in revised form 7 June 2011
Accepted 22 June 2011
Available online 10 August 2011

Keywords:

Groundwater remediation
Hydraulic conductivity
Permeable reactive barrier
Pumice
Zero-Valent Iron

ABSTRACT

This paper presents the results of laboratory column tests aimed at defining the optimum weight ratio of Zero-Valent Iron (ZVI)/Pumice granular mixtures to be used in Permeable Reactive Barriers (PRBs) for the removal of nickel from contaminated groundwater. The tests were carried out feeding the columns with aqueous solutions of nickel nitrate at concentrations of 5 and 50 mg/l using three ZVI/Pumice granular mixtures at various weight ratios (10/90, 30/70 and 50/50), for a total of six column tests; two additional tests were carried out using ZVI alone. The most successful compromise between reactivity (higher ZVI content) and long-term hydraulic performance (higher Pumice content) seems to be given by the ZVI/Pumice granular mixture with a 30/70 weight ratio.

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1. Introduction

Contaminated groundwater remediation by Permeable Reactive Barriers (PRBs) is an advanced technology with a large number of field applications located especially in the USA and Canada.

A PRB consists of a permeable subsurface diaphragm filled with the reactive medium; it 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. The medium most widely used in PRBs is the Zero-Valent IronTM (ZVI), which has proven very efficient, in particular, for heavy metals (Ni, Cu, Zn, etc.) removal [1,2].

ZVI can activate a variety of reaction mechanisms for contaminant removal (i.e. redox reactions, precipitation, and sorption). In particular, nickel can participate in a spontaneous electrochemical cementation process that involves the reduction of the more electropositive species ($E_{\text{Ni}^{2+}/\text{Ni}} = -0.264 \text{ V}$) by the more electronegative metal ($E_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$) [3]. Nickel can also be removed by precipitation as the metal hydroxide or by coprecipitation on iron corrosion products [4–7]. Therefore nickel removal

is possible in three different sites: on the ZVI surface, within the corrosion products film and on the surface of corrosion products.

Unfortunately, the use of ZVI alone as a reactive medium in PRBs revealed some drawbacks related to the long-term efficiency decrease due to the clogging of the barrier pores [5,8–12] by the precipitates (mainly hydroxides and salts such as carbonates) resulting from iron corrosion. The reduction of the permeability of the PRB 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.

Recently [5], in order to sustain hydraulic conductivity in the long-term and to optimize the use of ZVI, which is also rather expensive, the adoption in PRBs of granular mixtures of ZVI and pumice in different weight ratios, has been proposed.

Pumice is a natural complex silicate of volcanic origin [5,13], it has a significant surface chemical activity due to the presence of –OH groups and mono and polyvalent ions in its chemical structure. It presents a limited intrinsic nickel removal capacity most probably due to the ionic exchange with alkaline and alkaline-earth metals present in the pumice structure [5]. Moreover, according to the results of the research activity carried out on the ZVI/Pumice granular mixtures [5], 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. In fact, iron corrosion products can remove the pollutants by reduction (through Fe^{2+} or electron transfer at the surface of corrosion products), adsorption onto corrosion products, or coprecipitation

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[4–7]. The storage of iron corrosion products in the pumice pores allows, at the same time, the preservation of the hydraulic conductivity. The ZVI/pumice mixture guaranteed the maintaining of permeability for a period longer than ZVI alone with a specific removal efficiency higher than that of ZVI alone [5].

This paper presents the results of a series of column tests aimed at evaluating the optimal weight ratio between iron and pumice in nickel removal from contaminated groundwater in order to balance the preservation of the hydraulic conductivity (favoured by increasing the pumice content of the mixture) and the removal efficiency (favoured by increasing ZVI content).

2. Materials and methods

2.1. Experimental setup

The ZVI used in this research is of the type FERBLAST RI 850/3.5, distributed by Pometon S.p.A., Mestre, Italy. The reagent is composed mainly of ZVI (>99.74%), with impurities made up mainly of Manganese (about 0.26%) and traces of oxygen, sulphur and carbon.

The pumice used in this research comes from the quarries of Lipari (Aeolian Islands, Sicily, Italy), it is made up mainly of silica (SiO_2 – 71.75%) and by oxides of various elements (e.g. Al_2O_3 , K_2O , Na_2O , Fe_2O_3 , MgO) [5,13].

In this research column tests (see Fig. 1), performed by making a contaminated solution flow through a polymethyl methacrylate column filled with the selected reactive medium, were used in order to reproduce as realistically as possible the conditions of a real PRB in terms of flow and contact time. Each column was equipped with several sampling ports between inlet and outlet. The test solutions used in column tests were obtained by mixing nickel nitrate with distilled water (Nickel(II) nitrate hexahydrate, purity 99.999;

Sigma–Aldrich). The tests (see Table 1) were performed updraft by feeding a constant flow equal to 0.5 ml/min of nickel solution at concentrations respectively of 5 and 50 mg/l by using a precision peristaltic pump (Ismatec ISM 930). Three granular mixtures of ZVI and Pumice (50:50, 30:70 and 10:90 mass ratio respectively) were used as reactive media; moreover two additional column tests using ZVI alone were carried out as benchmarks. In particular, using 50 mg/l nickel solution and ZVI alone, only 240 g of the latter (the same quantity of ZVI used in the corresponding test carried out with 30:70 granular mixture) were used to make the comparison of the results easier.

The columns used were 50 cm long; only the tests carried out using a 50 mg/l nickel contaminating solution and a 10/90 ZVI/Pumice granular mixture and a 5 mg/l solution and ZVI only were carried out using columns 100 cm long. Longer columns were used to ascertain if an increase of the thickness of the reactive layer can proportionally increase nickel removal.

In order to assess the capacity of the mixtures to maintain an adequate permeability in the long-term, during column tests, several measurement of the hydraulic conductivity were carried out by the constant head permeability method [14]. Liquid specimens for chemical analyses were collected from sampling ports at fixed times (120 h, 1440 h, 3240 h).

At the end of the tests carried out using the 50 mg/l nickel solution, the columns containing the ZVI alone and the 30/70 ZVI/Pumice granular mixture were flushed with distilled water in order to detect any possible release of the contaminant removed; the test duration was 1518 h.

The evaluation of the contaminant concentrations in the specimens withdrawn during column tests was carried out by Atomic Absorption Spectrophotometry (AAS, Shimadzu AA-6701F) using Italian Standard Methods [15]. The standard method adopted

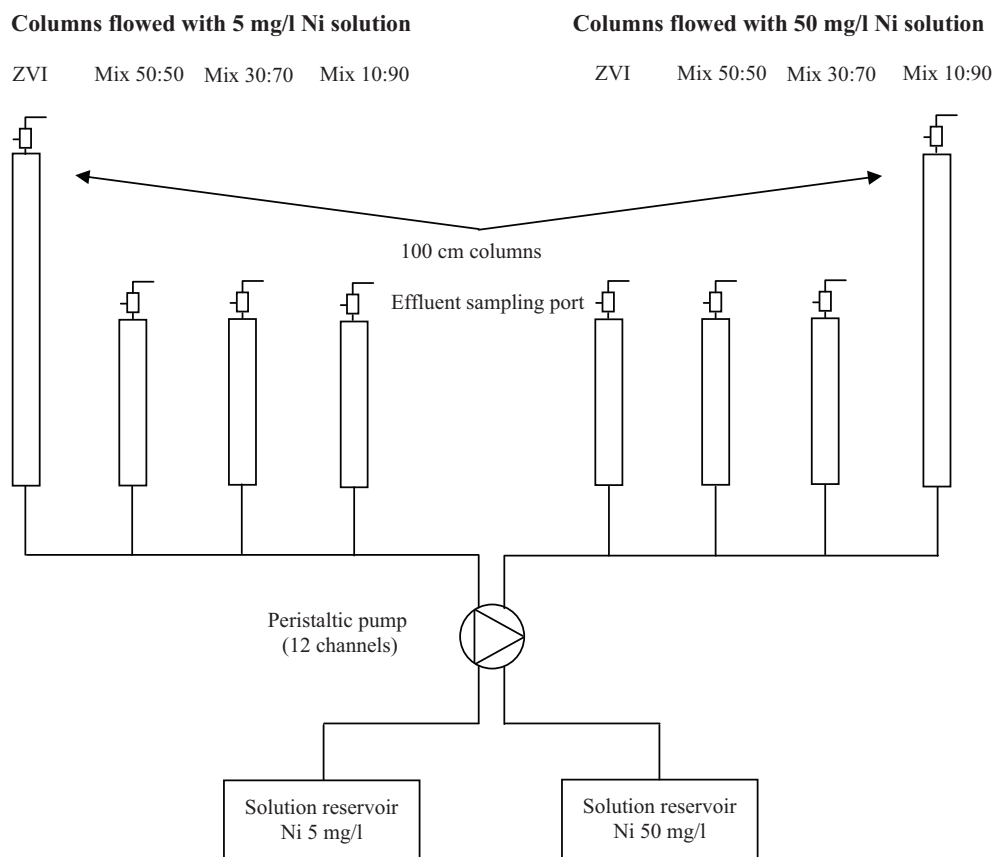


Fig. 1. Schematic diagram of experimental setup.

Table 1
Column tests program.

Contaminant	Reactive medium (weight ratio)	Weight (g)	ZVI (g) Pumice (g)	Volume (cm ³)	Porosity (%)	Pore volume (cm ³)	Q (cm ³ /min)	Residence time (h)	Normalized residence time (h/cm ²)
Ni 5 mg/l	ZVI–Pumice (10:90)	657.5	65.75 591.75	981.25	69	677.02	0.5	22.57	0.023
Ni 5 mg/l	ZVI–Pumice (30:70)	778.2	233.46 544.74	981.25	69.2	679.22	0.5	22.64	0.023
Ni 5 mg/l	ZVI–Pumice (50:50)	1035.3	517.65 517.65	981.25	67	656.65	0.5	21.89	0.022
Ni 5 mg/l	ZVI	7850 ^a	7850	1962.3 ^a	49.17	965.04	0.5	32.16	0.016
Ni 50 mg/l	ZVI–Pumice (10:90)	1526.2 ^a	152.62 1373.58	1962.5 ^a	64	1256.32	0.5	41.88	0.021
Ni 50 mg/l	ZVI–Pumice (30:70)	814.6	244.38 570.22	981.25	67.8	665.09	0.5	22.17	0.023
Ni 50 mg/l	ZVI–Pumice (50:50)	1062.3	531.15 531.15	981.25	66	648.18	0.5	21.61	0.022
Ni 50 mg/l	ZVI	240 ^b	240	58.87	48.20	28.38	0.5	0.94	0.016

^a 100 cm column, results refer to the samplings at 50 cm from the inlet.

^b Only the first 3 cm of the column were occupied by ZVI, the remaining space was filled by quartz gravel.

prescribes that flame determination can be used for nickel concentrations between 0.2 and 5 mg/l (precision 0.02 mg/l; dilution of the sample is mandatory for concentrations higher than 5 mg/l) while a graphite furnace must be used for nickel concentrations up to 0.04 mg/l (dilution is used for concentrations between 0.04 and 0.2 mg/l). The same method recommends the use of 1000 mg/l Ni standard solution for the plotting of the calibration curve (at least four points are used).

Due to the relative high complexity of the setup used in the experiments presented in this paper, in order to assess if the results obtained by the column tests setup are repeatable, for the experiments carried out using the Ni 50 mg/l contaminated solution and the 10:90 and 50:50 granular mixtures, two additional replicates per experiment (duration 120 h) were made. Table 2 reports the concentration measured, the average value and the standard variation for each set of experiments. The analysis of these results confirms the repeatability of that the results obtained by the experimental setup used in the experiments presented in this paper.

2.2. Calculation of the removal efficiency and of the specific removal

After the analyses, in order to evaluate the capacity of the different reactive media to remove nickel from contaminated groundwater, removal efficiency and specific removal were calculated.

Removal efficiency was defined as follow:

$$\text{removal_efficiency} = \frac{M_{\text{rem}}}{M_{\text{in}}} \times 100$$

where M_{rem} is the mass of contaminant removed, calculated by a mass balance, and M_{in} is the mass of contaminant flowed in the column.

The specific removal was defined as follow:

$$\text{Specific_removal} = \frac{M_{\text{rem}}}{M_{\text{react.medium}}} \times 100$$

where $M_{\text{react.medium}}$ is the mass of reactive medium used in the column.

3. Results and discussion

Figs. 2–4 show the column tests results in term of variation in the relative concentration of the contaminant along the columns filled

with the ZVI/Pumice granular mixtures over time (120 h, 1440 h, 3240 h); while Fig. 5 shows the results obtained in the tests carried out using ZVI alone (120 h and 1440 h). Table 3 resumes the interpretation of the experimental results for the three granular mixtures in terms of removal efficiency and specific removal.

Table 4 presents the results of the column release tests carried out at the end of the experiments in order to verify the stability of the contaminant removal. In particular, the total mass of nickel present in the pores at the end of the experiment with the contaminated solution (Ni_{PORES}), the amount of nickel leached both after the passage of one pore volume of distilled water (Ni_{1PV}) and at the end of the test (Ni_{TOT}) are reported. The results seem to indicate that the stability of the nickel removal by the granular mixture is higher than that exhibited by ZVI. In fact, even if the total mass released is similar in both the tests, the amount leached from ZVI was about 6 times higher than that present in the pores at the end of the column test carried using the contaminated solution while nickel released from the column containing the granular mixture was about half of that present in the pores.

The interpretation of column test results was carried out in terms of:

1. Variation in the relative concentration of the contaminant (C/C_0 ; where C is the measured contaminant concentration at a sampling port and C_0 is the same concentration at the inlet) along the column over time (120 h, 1440 h, and, for the granular mixtures only, 3240 h);
2. Comparison of the removal efficiency over time (120 h, 1440 h, and, for the granular mixtures only, 3240 h);
3. Specific pollutant removal (mass of pollutant removed for each gram of reactive medium);

3.1. Variation in the relative concentration of the contaminant

All the reactive media tested using the 5 mg/l nickel solution (Figs. 2a, 3a, 4a, 5a) allowed to attain the limit concentration (0.02 mg/l) required by Italian Regulation [16], nevertheless 10:90 ZVI–Pumice granular mixture barely reached it (Fig. 2a). For the other two granular mixtures tested (30:70 and 50:50 weight ratio), Figs. 3a and 4a, the limit concentration (0.02 mg/l) was already reached at the second sampling port (1.5 cm from the inlet). The performance of ZVI alone (Fig. 5a) is comparable with 30:70 and 50:50 granular mixtures although a significant higher amount of reagent was used.

Table 2
Analysis of the repeatability of column tests.

Contaminant	Reactive medium (weight ratio)	Outlet Conc. Experiment 1 (mg/l)	Outlet Conc. Replicate 1 (mg/l)	Outlet Conc. Replicate 2 (mg/l)	Average (mg/l)	Standard deviation (mg/l)	Standard dev./average (%)
Ni 50 mg/l	ZVI–Pumice (10:90)	6.01	5.33	7.07	6.133	0.878	14%
Ni 50 mg/l	ZVI–Pumice (50:50)	0.20	0.21	0.20	0.203	0.006	3%

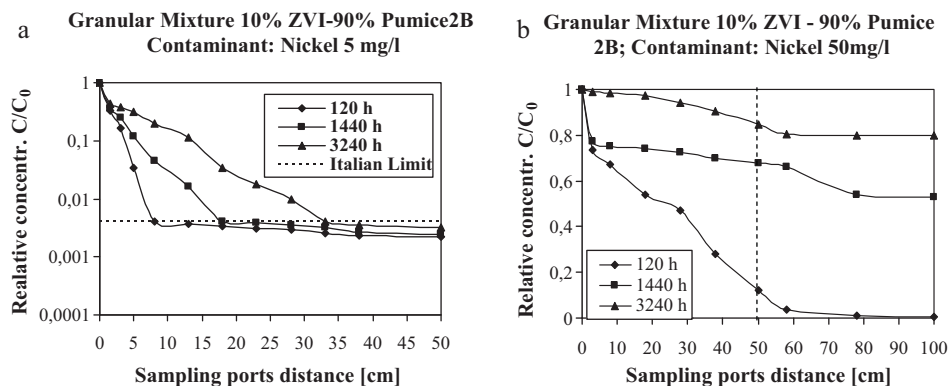


Fig. 2. Variation of relative nickel concentration for columns filled with 10/90 ZVI/Pumice granular mixture for an initial concentration of 5 mg/l (a) and 50 mg/l (b).

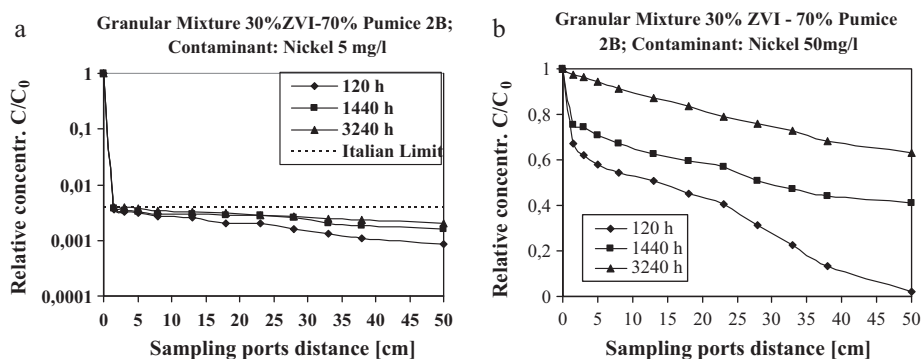


Fig. 3. Variation of relative nickel concentration for columns filled with 30/70 ZVI/Pumice granular mixtures for an initial concentration of 5 mg/l (a) and 50 mg/l (b).

For the tests carried out using a 50 mg/l nickel contaminating solution (Figs. 2b, 3b, 4b, 5b) none of the reactive media tested was able to reach the limit concentration stated by Italian Regulation [16], this is certainly due to the extremely high concentration of the influent solution (2500 times the limit concentration stated by relevant Regulation); in these cases it is possible that a significant increase of the column length would not have been sufficient to

reach and maintain the required concentration. Only the 50:50 and 30:70 granular mixtures (Figs. 3b and 4b) were able to get near the limit concentration but after only 120 h of test and in this case an increase of the treatment zone length would have probably been beneficial.

This is at least partially confirmed by the results shown in Fig. 2b, where the test carried out using a 10:90 granular mixture, a 50 mg/l

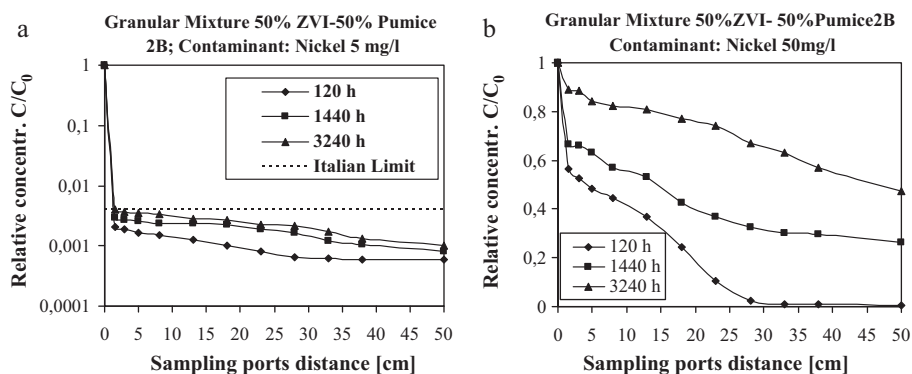


Fig. 4. Variation of relative nickel concentration for columns filled with 50/50 ZVI/Pumice granular mixtures for an initial concentration of 5 mg/l (a) and 50 mg/l (b).

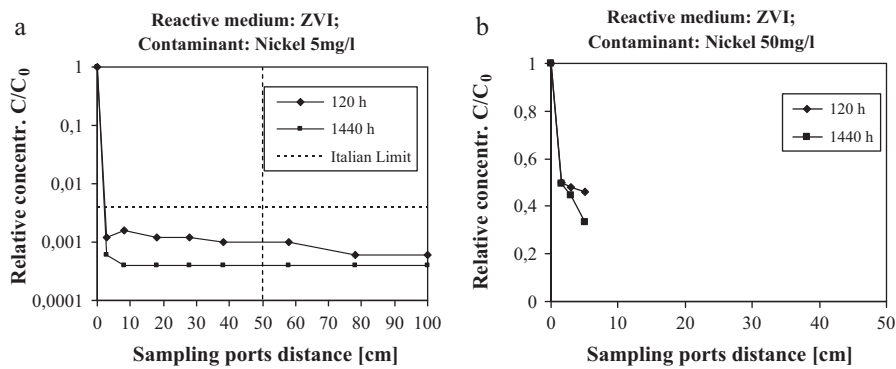


Fig. 5. Variation of relative nickel concentration for columns filled with ZVI for an initial concentration of 5 mg/l (a) and 50 mg/l (b).

Table 3

Granular mixtures removal efficiency and specific removal of contaminant after respectively 120, 1440 and 3240 h after the beginning of the experiment.

Contaminant	Reactive medium (weight ratio)	Weight (g)	ZVI (g) Pumice (g)	Volume (cm ³)	Removal efficiency (%)			Specific removal (g _{contaminant} /g _{reactive medium})		
					120 h ^a	1440 h ^a	3240 h ^a	120 h ^a	1440 h ^a	3240 h ^a
Ni 5 mg/l	ZVI–Pumice (10:90)	657.5	65.75 591.75	981.25	99.13	99.72	99.70	2.71E–05	3.28E–04	7.37E–04
Ni 5 mg/l	ZVI–Pumice (30:70)	778.2	233.46 544.74	981.25	99.60	99.85	99.83	2.30E–05	2.77E–04	6.23E–04
Ni 5 mg/l	ZVI–Pumice (50:50)	1035.3	517.65 517.65	981.25	99.65	99.90	99.90	1.73E–05	2.08E–04	4.69E–04
Ni 5 mg/l	ZVI	7850 ^b	7850	1962.3 ^b	99.94	99.96	–	3.2E–06	1.97E–05	–
Ni 50 mg/l	ZVI–Pumice (10:90)	1526.2 ^b	152.62 1373.58	1962.5 ^b	79.98	61.43	40.48	1.08E–04	1.04E–03	1.63E–03
Ni 50 mg/l	ZVI–Pumice (30:70)	814.6	244.38 570.22	981.25	91.50	79.06	61.53	2.02E–04	2.10E–03	3.67E–03
Ni 50 mg/l	ZVI–Pumice (50:50)	1062.3	531.15 531.15	981.25	96.28	87.06	73.57	1.63E–04	1.77E–03	3.37E–03
Ni 50 mg/l	ZVI	240 ^c	240 ^c	58.87	53.00	32.7	–	1.68E–04	2.66E–03	–

^a Elapsed time (h) from the beginning of the experiment.

^b 100 cm column, results refer to the samplings at 50 cm from the inlet.

^c Only the first 3 cm of the column were occupied by ZVI, the remaining space was filled by quartz gravel.

nickel solution and a 100-cm long column (as already mentioned, the other tests were carried out using 50 cm columns) were used. In this case it is possible to verify that the performance of the column in term of relative concentration at 100 cm from the inlet was higher than that at 50 cm from the inlet. On the contrary, in agreement with the results shown in Fig. 5a for the test carried out using ZVI alone and a 5 mg/l solution, the increase in column length was not significantly beneficial. From the analysis of Figs. 2–4, especially for the tests carried out using the 50 mg/l nickel contaminating solution, it is evident that the removal capacity of the reactive medium was progressively reduced. The analysis of the behaviour of the three granular mixtures tested show that the performances of 30:70 and 50:50 mixtures (Figs. 3 and 4) are comparable, even though, thanks to the higher content of iron, the column filled with the 50:50 granular mixture performs better in terms of the final concentration attained (about 30% lower on average for the 50:50 granular mixture respect to 30:70 one but the iron content of the 50:50 granular mixture is more than 60% greater than the 30:70 one).

Table 4

Results of the release test.

Reactive material	Ni _{PORES} (g)	Ni _{IPV} (g)	Ni _{TOT} (g)
ZVI	0.0012	0.0057	0.0071
30/70 ZVI/Pumice Mix	0.0139	0.0037	0.0065

The column test carried out using the 50 mg/l nickel solution and 240 g of ZVI (Fig. 5b) allows a direct comparison with the corresponding test carried out using the 30:70 granular mixture; it reveals a clear advantage in the use of the mixture compared to when similar quantities of ZVI are used alone; this advantage is probably linked mainly to the increased residence time and as already mentioned, to the pumice capacity of storing corrosion products in its pores augmenting the available reactive surface for the reactions between the contaminant and the iron oxides [5].

3.2. Comparison of the removal efficiency and of the specific removal

According to the results presented in Table 3, the nickel removal from the columns flushed with the 5 mg/l nickel solution is almost complete (>99%) and for this reason the highest specific removal is exhibited by the 10:90 granular mixture, since it removes the same amount of pollutant using a smaller mass of reactive medium. There is not a noticeable difference between the performance of granular mixtures and ZVI alone. On the other hand, in this case, the performance of ZVI alone is clearly modest, in fact, although the amount of ZVI used is about 15 times higher than that of the 50:50 granular mixtures, the nickel removal is comparable but with a large waste of ZVI as witnessed by the low specific removal.

Using a 50 mg/l contaminating solution and considering the 1400 and 3240 h, time horizons, results are different; in this case the pollutant removal is not complete and the performance of

30:70 and 50:50 granular mixtures is significantly higher than that exhibited by 10:90 one and by ZVI alone. Moreover, the removal efficiency of 50:50 granular mixture is on average 20% higher than that of the 30:70 mixture, while the latter performs better in term of specific removal, indicating a most efficient use of iron.

Long-term permeability tests carried out at the end of the tests showed that initial permeability of granular mixtures (in the order of 10^{-3} cm/s) was substantially preserved, reporting only a slight reduction of less than one order of magnitude only for granular mixtures with the highest ZVI/Pumice weight ratio and permeated with the most concentrated nickel solution.

4. Conclusions

In order to mitigate the problems related to the long-term efficiency of ZVI PRBs, the use of granular mixtures of ZVI and pumice has been recently proposed; several column tests were carried out to select the best ZVI/Pumice weight ratio for the granular mixture for nickel removal.

The analysis of the results of column tests demonstrated that:

- all the reactive media tested could remove nickel below Italian Standard from groundwater starting from an initial concentration of 5 mg/l;
- for the tests carried out using a contaminant solution with an initial concentration of 50 mg/l none of the reactive media tested were able to reach the concentration set by Italian Regulation but, although the 50:50 granular mixture presents a better performance, the 30:70 one gives comparable results especially if it is taken into account the fact that in this latter the amount of ZVI used is less than a half of that used in the 50:50 mixture;
- granular mixtures guarantee a most efficient use of ZVI compared to when it is used alone;
- the performance of the granular mixture is enhanced if the ZVI/Pumice weight ratio is high (74% removal at the outlet of the column for the 50:50 mixture, 62% for the 30:70 and 40% for the 10:90 after 3240 h using the 50 mg/l nickel solution).
- the best compromise between reactivity and long-term preservation of hydraulic conductivity is probably given by the 30:70 granular mixture.

Acknowledgement

The authors wish to thank Dott. Stefania Bilardi for her contribution in revising this paper.

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