Optimal design of ZVI/lapillus mixtures for nickel removal in permeable reactive barriers

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ABSTRACT

The remediation of contaminated groundwater, through the technology of permeable reactive barriers (PRB), involves the use of a reactive medium able to reduce the concentration of contaminants as long as remediation targets are achieved. In the present study, the use of granular mixtures composed of zero valent iron (ZVI) and lapillus for the treatment of nickel contaminated groundwater is proposed. Through short and long term column experiments, the effects of the following were analysed: i) ZVI percentage per unit volume, ii) reactive medium thickness, iii) flow velocity and iv) initial nickel concentration, on the breakthrough point occurrence (point where a rapid increase in nickel concentration in the effluent is observed). The optimal mixture composition (i.e. the optimal ZVI content per unit volume) was defined when the reactive medium was able to keep its reactivity and hydraulic conductivity for the time necessary for remediation. This capacity, as shown in this study, depends on the propagation velocity of the contamination front through the reactive medium.

Keywords: breakthrough point, groundwater, hydraulic conductivity, retardation factor

1 INTRODUCTION

A permeable reactive barrier (PRB) consists of the placement of a granular reactive medium in the subsoil in order to intercept a contaminated plume and remove the contaminants within.

The placement of the reactive material in the subsoil, downstream of the contamination source, defines the configuration of the barrier. In particular, the most used configuration of the barrier is obtained (horizontal PRB) by arranging the reactive medium in a direction perpendicular to the groundwater flow. By placing the reactive medium between two impermeable diaphragms, the funnel and gate or the caisson configurations are obtained (Elder and Benson, 2019). In the funnel and gate configuration, elements with lower permeability direct the contaminated flow towards the reactive medium (the gate). In the caisson configuration, the reactive medium is installed between impermeable elements that force the contaminated plume to cross the reactive medium with a vertical upward flow.

Zero valent iron (ZVI) has been employed extensively for groundwater remediation (Li et al., 2019) since it is efficient in the removal of several contaminants. Notwithstanding of successful examples of application of this technology as the good performance observed after 15 years of operation of a PRB composed of ZVI (ZVI-PRB) and installed for the treatment of groundwater contaminated by chromate and trichloroethylene (Wilkin et al., 2014), there are several examples of ZVI-PRB failures. The causes of the progressive hydraulic conductivity reduction are related to the formation of mineral precipitates and iron corrosion products that fill the pores of the reactive medium causing the clogging of the PRB. For example, in two cases of full scale applications of ZVI-PRB, the hydraulic conductivity reduction was due to the presence of cemented zones within the PRB (Liang et al., 2001; EPA, 2002). In other cases, the hydraulic conductivity reduction was attributed to chemical clogging, due to the presence of mineral precipitates, such as calcium and iron carbonates, mostly located at the barrier inlet (Morrison, 2003; ITRC, 2011).

By products derived from iron corrosion, which cause the reduction of the hydraulic conductivity, can be solids, like iron oxides and hydroxides, and gaseous, like the hydrogen derived by anaerobic corrosion. Solid corrosion products have an expansive nature, i.e. the volume of the ZVI after corrosion is higher than that of the original metal (Moraci et al., 2016a).

Different numerical models are used in order to predict the hydraulic behaviour of a ZVI-PRB or to understand the phenomena leading to its porosity reduction. Some authors (Li et al., 2005, 2006; Komnitsas et al. 2006; O et al., 2009) attributed the cause
The hydraulic conductivity reduction to mineral precipitation. This phenomenon is linked not only to the site-specific geochemical and hydrogeological conditions but also to the iron corrosion rate (O et al., 2009). If gas production is also considered, numerical models results show that in certain cases hydraulic conductivity loss can be mainly attributable to gas production rather than to mineral precipitation (Henderson and Demond, 2011; Jeen et al., 2012; Moraci et al., 2016).

Granular reactive mixtures obtained by the combination of different materials have already been proposed in order to increase the long-term performance of the barrier by improving its long-term permeability, by providing multiple mechanisms for the removal of contaminants and/or by reducing costs of using single/pure granular materials (Obiri-Nyarko et al., 2014). In this context, we proposed the use of volcanic materials, i.e. pumice and lapillus, as admixing agents to be coupled with ZVI (Moraci and Calabrò, 2010; Calabrò et al., 2012; Moraci et al., 2015; Madaffari et al., 2017; Bilardi et al., 2019). A comparison between the two different granular mixtures showed as ZVI/ lapillus mixtures are more reactive than ZVI/pumice mixtures (Bilardi et al., in press).

In a granular reactive mixture (ZVI/pumice or ZVI/ lapillus), respect to a reactive medium composed of pure ZVI, the ZVI particles are more dispersed (per unit volume) thanks to the granular admixing agent (pumice or lapillus). Therefore, the fraction of voids, involved in the aforementioned phenomena of clogging, is lower and the granular reactive mixture is less subject to clogging.

This paper analyses the main results obtained by column tests carried out on granular mixtures of ZVI/ lapillus in order to define the optimal mixture for the removal of nickel under different conditions of flow velocity and contaminant concentration.

2 REACTIVE MEDIUM SELECTION

The choice of the most suitable reactive medium represents a key point for the correct implementation of this technology. This choice requires an in-depth knowledge of the reactive and hydraulic behaviour of the granular medium in the short and long term. First, the reactive medium should be compatible with the subsurface environment. It should not cause adverse chemical reactions or the production of undesired by-products when reacting with constituents in the contaminant plume and should not act as a possible source of contaminants itself (Faisal et al., 2018). In order to improve the sustainability of the remediation technology and reduce costs, it is desirable that the material is easily available, of low or moderate cost and safe to handle for the operators. An important parameter of the reactive medium is its grain size distribution that regulates the reactivity and the hydraulic conductivity of the barrier. The reactive medium should satisfy the filter design criteria (i.e. internal stability, retention and permeability criteria) in relation to the grain size distribution and permeability of the aquifer (Moraci et al., 2016b).

3 MATERIALS AND METHODS

The ZVI (Ferblast RI 850/3.5) and lapillus used in this study were purchased from Pometon S.p.A. (Mestre, Italy) and SEM “Società Estrattiva Monterosi” S.r.l. (Viterbo, Lazio) respectively.

Lapillus is a volcanic rock generated during explosive eruptions due to the vigorous escape of gases from lavas. It is a natural material and often is a by-product of pumice mining (Catalfamo et al., 2006) that is not subjected to any kind of physical or chemical treatment. It mainly consists of silica (SiO$_2$ = 47%) and oxides of various elements (Al$_2$O$_3$ = 15%, K$_2$O = 8%, Na$_2$O = 1%, Fe$_2$O$_3$-FeO = 7–8%, MnO = 0.15%, MgO = 5.5% and CaO = 11%).

The granular ZVI and lapillus are characterized by uniform grain size distributions (Figure 1). The coefficient of uniformity ($U = d_{60}/d_{10}$) is 2, for ZVI, and 3.2, for lapillus. The mean grain size ($d_{50}$) is 0.5 mm, for ZVI, and 0.4 mm, for lapillus.

![Fig. 1. Grain size distribution of the ZVI and lapillus used in the research.](image)

The column tests were carried out using polymethyl methacrylate (PMMA—Plexiglas™) columns with an internal diameter of 5 ± 0.1 cm and a height of 50 cm. The columns are equipped with several sampling ports located at different distances from inlet (i.e., 3, 8, 18, 28, 38 and 50 cm). A peristaltic pump (Watson Marlow 205S) was used to feed the columns, under constant upward flow. A scheme of the column test apparatus is showed in Figure 2.

Lapillus and ZVI were mixed at a prefixed weight ratio and the columns were 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. The contaminated aqueous solutions were prepared by dissolving nickel (II) nitrate hexahydrate (purity 99.999, Sigma-Aldrich, Germany) in distilled water in order to obtain the desired initial concentration.

During the column tests, performed at room temperature (20 ± 4 °C), the hydraulic conductivity was...
determined by the falling-head \((k < 1 \times 10^{-6} \text{ m/s})\) or constant-head \((k > 1 \times 10^{-6} \text{ m/s})\) permeability tests (Head and Keeton, 2008). Nickel concentration in the aqueous samples, collected during column tests, was determined using ICP-OES (Perkin Elmer OPTIMA 8000).

\[
\text{RC} = \frac{M_{\text{Ni-rem}}}{M_{\text{rm}}}
\]

(1)

where: \(M_{\text{Ni-rem}}\) is the mass of removed nickel calculated at the breakthrough point using a mass balance and \(M_{\text{rm}}\) is the mass of reactive medium calculated at the specific sampling port where the breakthrough was observed.

The retardation factor, \(R_f\), is defined through the following equation:

\[
R_f = \frac{v_{ct}}{v_{cont}}
\]

(2)

where: \(v_{ct}\) is the column test velocity that represents the inlet contaminant velocity calculated by dividing the flow rate used in the test by the area of the column, while \(v_{cont}\) is the average value of the propagation velocity of the contamination front through the reactive medium and it is calculated as follows:

\[
v_{cont} = \frac{1}{n} \sum_{i=1}^{n} \frac{L_i}{T_{bi}}
\]

(3)

where \(n\) is the number of sampling ports where the breakthrough point is observed and \(L_i\) is the reactive medium thickness (distance of the \(i\)-th sampling from column inlet) where the breakthrough is observed and \(T_{bi}\) is the breakthrough time at the \(i\)-th sampling port.

Table 1 summarizes the main data referred to column tests (i.e. weight ratio of the granular mixture, \(v_{ct}\), \(C_0\) that is the initial nickel concentration and test duration). Three different ZVI/lapillus (lap.) weight ratios (equal to 10:90, 30:70 and 50:50), three values of flow velocity (0.079, 0.4 and 1.9 m/day) and three values of the initial nickel concentration (10, 50 and 100 mg/L) were investigated in the research. The effect of the weight ratio was investigated using a concentration of 50 mg/L of nickel (Ni) and a flow velocity of 0.4 m/day. The flow velocity effect was investigated using the 30:70 granular mixture and a solution containing 50 mg/L of Ni. The effect of initial Ni concentration was investigated using the 30:70 granular mixture and a flow velocity of 0.4 m/day.

4 COLUMN TESTS RESULTS

Column test results are analysed in terms of breakthrough time \((T_b)\), removal capacity \((RC)\), ratio between the final \((k_f)\) and initial value \((k_0)\) of hydraulic conductivity \((k_f/k_0)\) and retardation factor \((R_f)\).

The breakthrough time, \(T_b\), for each sampling port, is identified as the time where a rapid increase of the contaminant concentration is clearly observed.

The removal capacity, \(RC\), is quantified through the following equation:

The effect of the weight ratio was investigated using a concentration of 50 mg/L of nickel (Ni) and a flow velocity of 0.4 m/day. The flow velocity effect was investigated using the 30:70 granular mixture and a solution containing 50 mg/L of Ni. The effect of initial Ni concentration was investigated using the 30:70 granular mixture and a flow velocity of 0.4 m/day.

Table 1. Main characteristics of the performed column tests.

| ID     | Reactive medium | \(v_{ct}\) [m/day] | \(C_0\) [mg/L] | Duration [days] |
|--------|-----------------|---------------------|----------------|-----------------|
| 1      | ZVI/lap. 10:90  | 0.4                 | 50             | 216             |
| 2      | ZVI/lap. 30:70  | 0.4                 | 50             | 250             |
| 3      | ZVI/lap. 50:50  | 0.4                 | 50             | 222             |
| 4      | ZVI/lap. 30:70  | 0.079               | 50             | 1223            |
| 5      | ZVI/lap. 30:70  | 1.9                 | 50             | 35              |
| 6      | ZVI/lap. 30:70  | 0.4                 | 10             | 502             |
| 7      | ZVI/lap. 30:70  | 0.4                 | 100            | 120             |

4.1 ZVI/lapillus mixtures at different weight ratios

Figure 3 shows the \(T_b\) values observed at the different sampling ports for the 10:90, 30:70 and 50:50 ZVI/lapillus granular mixtures.
Increasing the percentage of ZVI per unit volume of the granular mixture, an increase of the breakthrough time is observed. The 10:90 mixture shows the lowest values of $T_b$ that indicate a rapid advancement of the contaminated front and a faster depletion of the reactive medium than the other two mixtures.

Table 2 summarizes the $RC$ and the $k_f/k_0$ values calculated for each mixture. $RC$ is calculated at the outlet of the column ($L = 0.5$ m). $RC$ increases with the amount of ZVI present in the mixture but the increase is not proportional, in fact, a three-fold increase of ZVI guarantees a 35% higher $RC$ while a five-fold increase a 229% higher $RC$.

The hydraulic conductivity of the 50:50 mixture reduces of about two orders of magnitude compared to the initial value, while the best hydraulic behaviour is observed for the 10:90 mixture, which should guarantee a slightly higher permeability over the long term than the 30:70 mixture. The reduction in hydraulic conductivity observed for the 50:50 mixture, is linked to the higher ZVI content per unit volume of the column, and consequently, to the higher quantity of corrosion products and gases (Madaffari et al., 2017).

Table 2. Column test results for different ZVI/lapillus mixtures.

| Reactive medium   | $RC$ [mg/g] | $k_f/k_0$ |
|-------------------|-------------|-----------|
| ZVI/lap. 10:90    | 1.7         | 0.413     |
| ZVI/lap. 30:70    | 2.3         | 0.282     |
| ZVI/lap. 50:50    | 5.6         | 0.0351    |

4.2 Effect of flow velocity

Figure 4 shows $T_b$ values observed at the different sampling ports for the 30:70 mixture permeated under different flow velocities for a Ni concentration equal to 50 mg/L.

![Fig. 4. Breakthrough time ($T_b$) vs. reactive medium thickness ($L$) for three different flow velocities.](image)

When the flow velocity is increased of 5 times than the mean value (i.e. 0.4 m/day), a rapid depletion of the reactive medium is observed. While, a considerable increase of the reactive barrier lifetime is observed when the mean value of flow velocity is reduced of 5 times (from 0.4 m/day to 0.079 m/day).

Table 3 summarizes the $RC$ and the $k_f/k_0$ values calculated for each test, where $RC$ is calculated at the outlet ($L = 0.5$ m). Regarding mixture reactive behaviour, when flow velocity decreases, $RC$ grow due to an increase of the residence time as observed also in previous studies (Moraci et al., 2015). Moreover, at the end of the three tests significant variations of the hydraulic conductivity respect to the initial value are not highlighted (Madaffari et al., 2017).

Table 3. Column test results (effect of flow velocity).

| $v_f$ [m/day] | $RC$ [mg/g] | $k_f/k_0$ |
|---------------|-------------|-----------|
| 0.079         | 3.6         | 0.193     |
| 0.4           | 2.3         | 0.282     |
| 1.9           | 0.84        | 0.92      |

4.3 Effect of Ni concentration

Figure 5 shows $T_b$ values observed at the different sampling ports for the 30:70 mixture permeated by different initial Ni concentrations for a flow velocity equal to 0.4 m/day.

![Fig. 5. Breakthrough time ($T_b$) vs. reactive medium thickness ($L$) for three different Ni concentrations.](image)

For the highest value of Ni concentration (i.e. 100 mg/L), the breakthrough occurs quickly at each sampling port. While, for the lowest value of Ni concentration (i.e. 10 mg/L), breakthrough is observed only at the first sampling port ($L = 0.03$ m) after 73 days and at the second sampling port ($L = 0.08$ m) after 294 days.

Table 4 summarizes the $RC$ and the $k_f/k_0$ values calculated in each test. The $RC$ value for the column test carried out using the lowest Ni concentration is calculated for a thickness of 0.08 m. While, for the other two column tests $RC$ is calculated at the outlet ($L = 0.5$ m). $RC$ increases as the initial Ni concentration decreases. In particular, halving the concentration (from 100 to 50 mg/L) the $RC$ value, calculated at the outlet,
increases about 5 times.

The column showing the best hydraulic behaviour is the one permeated with the highest value of initial Ni concentration (i.e. 100 mg/L). While, a decrease of the hydraulic conductivity of about three orders of magnitude with respect to the initial value for the column test performed with Ni 10 mg/L is observed (Madaffari et al., 2017). In this latter case, the $k/k_0$ value refers to the end of the test (502 days) for a cumulated mass of nickel in input 2.4 times less than that in the other two columns.

Table 4. Column test results (effect of Ni concentration).

| Ni [mg/l] | RC [mg/g] | k/k_0 |
|-----------|-----------|-------|
| 10        | 8^a       | 0.00413 |
| 50        | 2.3       | 0.282  |
| 100       | 0.47      | 0.857  |

*a*Calculated for $L = 0.08$ m

4.4 Correlation between hydraulic conductivity and the retardation factor

$R_f$ values, calculated for each column test (Table 1), are correlated with the corresponding $k/k_0$ values in Figure 6. A decrease of the hydraulic conductivity with the increase of $R_f$ is observed in all performed column tests. Therefore, the retardation factor could be a good indicator of the reactive and hydraulic performance of the reactive medium. In fact, considering $R_f$ values, the reactive and hydraulic behaviour of the investigated ZVI/lapillus granular mixtures could be classified into the following categories:

I. $R_f < 50$ (Tests 5 and 7): fast reactivity depletion and optimal long term hydraulic behaviour;
II. $50 < R_f < 100$ (Tests 1, 2 and 4): good compromise between reactivity and long term hydraulic conductivity;
III. $R_f > 100$ (Tests 3 and 6): optimal reactivity and considerable long term hydraulic conductivity reduction.

For column tests 3 and 6 the possible solution in order to avoid long term hydraulic conductivity reduction, is to adopt a lower value of ZVI per unit of volume. This solution could be also limited to the entrance zone of the barrier, where clogging phenomenon frequently occurs. Therefore, using these two solutions, a decrease of the $R_f$ value occurs and therefore also the risk of chemical clogging is reduced.

5 CONCLUSIONS

The optimal mixture composition to be used as reactive medium in a PRB (i.e. the optimal ZVI content per unit volume) is the one able to keep its reactivity and hydraulic conductivity for the design lifetime (the time necessary for remediation).

For the ZVI/lapillus granular mixtures to be used for the remediation of Ni contaminated groundwater, the increase of the ZVI content per unit volume guarantees higher level of reactivity, while if ZVI particles are dispersed in a greater volume, the hydraulic conductivity is better preserved.

The optimal composition of the ZVI/lapillus mixture that guarantees the best compromise between reactivity and hydraulic conductivity of the PRB depends on in situ conditions (flow velocity and Ni initial concentration).

In this study, the use of $R_f$, a parameter easy to determine and useful to identify the attitude of the reactive medium to quickly reduce its reactivity or hydraulic conductivity, is proposed. This parameter is the retardation factor that represents the propagation velocity of the contamination front respect to the velocity in a not reactive medium. It is clear that higher values of $R_f$ are representative of an optimal reactive behaviour of the granular ZVI/lapillus mixtures but also of a faster reduction of the hydraulic conductivity for this reason a range of values giving the optimal compromise between reactivity and preservation of hydraulic conductivity has been proposed.

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