ARTICLE IN PRESS

Available online at www.sciencedirect.com

ScienceDirect

Soils and Foundations xxx (2017) xxx–xxx

www.elsevier.com/locate/sandf

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

Maria Grazia Madaffari, Stefania Bilardi, Paolo S. Calabrò, Nicola Moraci *

Department of Civil, Energy, Environment and Materials Engineering (DICEAM), Mediterranea University of Reggio Calabria, Reggio Calabria, Italy

Received 8 July 2016; received in revised form 12 April 2017; accepted 28 May 2017

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.

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

Peer review under responsibility of The Japanese Geotechnical Society.

* Corresponding author at: Via Graziella loc, Feo di Vito, 89122 Reggio Calabria, Italy.

E-mail addresses: mariagrazia.madaffari@unirc.it (M.G. Madaffari), stefania.bilardi@unirc.it (S. Bilardi), paolo.calabro@unirc.it (P.S. Calabrò), nicola.moraci@unirc.it (N. Moraci).

https://doi.org/10.1016/j.sandf.2017.08.006

0038-0806/© 2017 Production and hosting by Elsevier B.V. on behalf of The Japanese Geotechnical Society.

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) (Rangsivek 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 ($E^0_{Ni(II)/Ni(0)} = -0.25$ V; $E^0_{Fe(II)/Fe(0)} = -0.44$ 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 g/cm^3.

The granular lapillus was distributed by SEM "Società Estrattiva Monterosi" s.r.l., Viterbo, Italy. It mainly consisted of silica ($SiO_2 = 47\%$) and oxides of various elements ($Al_2O_3 = 15\%$, $K_2O = 8\%$, $Na_2O = 1\%$, Fe_2O_3-$FeO = 7$–8%, $MnO = 0.15\%$, $MgO = 5.5\%$ and $CaO = 11\%$).

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 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

Please cite this article in press as: Madaffari, M.G. et al., Nickel removal by zero valent iron/lapillus mixtures in column systems, Soils Found. (2017), https://doi.org/10.1016/j.sandf.2017.08.006