Scuola di Dottorato
Università degli Studi *Mediterranea* di Reggio Calabria

Dipartimento Di Meccanica e Materiali

Dottorato di Ricerca in
Ingegneria Geotecnica e Chimica dei Materiali

S.S.D. ICAR/07
XXIV ciclo

SHORT AND LONG TERM BEHAVIOUR OF Fe^0 AND Fe^0/PUMICE GRANULAR MIXTURES TO BE USED IN PRB FOR GROUNDWATER REMEDIATION

Dottoranda:
Stefania Bilardi

Tutor:
Prof. Ing. Nicola Moraci

Ing. Paolo S. Calabrò

Coordinatore:
Prof. Ing. Nicola Moraci

Reggio Calabria, Gennaio 2012

STEFANIA BILARDI

SHORT AND LONG TERM BEHAVIOUR OF Fe^0 AND Fe^0/PUMICE GRANULAR MIXTURES TO BE USED IN PRB FOR GROUNDWATER REMEDIATION

Il Collegio dei docenti del Dottorato di Ricerca in
Ingegneria Geotecnica e Chimica dei materiali
è composto da:

Moraci Nicola (Coordinatore)
Antonucci Pier Luigi
Dente Giovanni
Donato Andrea
Mastrorilli Pietro
Messina Giacomo
Nobile Francesco Cosimo
Pietropaolo Rosario
Silvestri Francesco
Valore Calogero
Conte Enrico
Giovine Pasquale
Musolino Maria Grazia
Nocilla Nicola
Santangelo Saveria
Airò Farulla Camillo
Calabro' Paolo Salvatore
Candito Pasquale
Cotronei Maria Antonia
Faggio Giuliana
Frontera Patrizia
Gallo Vito
Mortara Giuseppe
Porcino Daniela Dominica
Ziccarelli Maurizio

Ringraziamenti:
Ringrazio i miei tutor, il Prof. Nicola Moraci e l'ing. Paolo S. Calabrò, che con la loro passione, esperienza e professionalità mi hanno guidata nel corso della ricerca.
Ringrazio il dott. Giuseppe Panzera e il Sig. Michelangelo Malara per la loro preziosa e costante disponibilità offerta durante le attività sperimentali della ricerca svolte presso i laboratori di chimica e di geotecnica.
Ringrazio l'Ing. Paolo Suraci, collega e collaboratore dell'attività di ricerca presentata nella tesi, per il suo aiuto ed i suoi consigli.
Ringrazio tutti i colleghi Laura C., Lidia C., Diego F., Enzo M., Giuseppe C., Domenico G., Domenico I., Maria Clorinda M., Grazia F. e Maria Grazia M. con i quali ho condiviso le mie giornate lavorative.
Ringrazio i miei genitori, mia sorella e mio marito che con il loro amore e la loro inesauribile pazienza mi hanno sostenuto in tutti i momenti.

On cover:
SEM images of the pumice particles (B)
and of the ZVI particles (A)

TABLE OF CONTENTS

6. BATCH TESTS: RESULTS AND DISCUSSION 51

7. COLUMN TESTS: SINGLE-METAL SOLUTIONS 63

8. COLUMN TESTS: THREE-CONTAMINANTS SOLUTIONS 101

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

1.1 Groundwater remediation

Groundwater is an important resource for our planet, in fact it stores about 95% per cent of the world's available fresh water. Unfortunately the quality of groundwater is affected by population growth and industrialization.

The possible sources that can contaminate groundwater are numerous but as examples landfills, leaking gasoline storage tanks, leaking septic tanks, and accidental spills can be cited according to scientific literature. The more significant contaminant sources are leachates coming from mine tailings or landfills not correctly designed. Leachates may contain a number of toxic chemical like heavy metals and metalloids such as arsenic, cadmium, chromium, copper, iron, mercury, molybdenum, nickel, lead, selenium, uranium and zinc.

The traditional technology for groundwater remediation is constituted by "pump and treat" systems. These systems extract groundwater to the surface and after treatment re-introduce it to the subsurface or discharge it to a receiving water body. Such approaches are energy and maintenance intensive. More importantly, they are often ineffective: a National Research Council study found that 69 of 77 treatment sites using pump and treat had not met their clean-up goals (Henderson, 2007). A relatively recent technology alternative to the traditional pump and treat are the permeable reactive barriers (PRBs).

1.2 Groundwater remediation through permeable reactive barriers

A PRB is a promising groundwater remediation technology, it consists of a permeable wall filled with a reactive medium installed perpendicularly to groundwater flow. As contaminated water flows through the barrier under its natural hydraulic gradient the reactive medium degrade or trap the contaminants within. Compared to other remediation technologies, a PRB may offer several advantages. First it eliminates the need for above-ground management of both large volumes of water containing low concentrations of contaminants and the waste generated from the treatment of such water (Blowes et al., 1999). Secondly, because water flows under its natural gradient, there is no energy input required.

Operational costs include monitoring and possible replacement/regeneration of the reactive medium.

The first permeable reactive barrier was installed in 1994 at the Intersil Site in Sunnyvale, California (USA), to treat chlorinated solvents. It used 100% zero-valent iron (ZVI) in its reactive zone and, as documented by Henderson and Demond (2007), it was still meeting its clean-up goals in the year 2004. With the initial success of PRBs, their use has become more widespread. Indeed, PRBs have been installed to treat organics, heavy metals, radionuclides, and nutrients (RTDF, 2002), with nearly 50% treating organic contaminants and nearly 20% treating metals as of 2002 (EPA, 2002). Typical reactive media used in the field include zero-valent iron (ZVI), cast iron, steel wool, amorphous ferric oxide, phosphate, zeolite, activated carbon, limestone (see Scherer et al. 2000); however, of the over 200 PRBs installed worldwide before the year 2004, 120 are iron-based (90 in the USA) (ITRC, 2005; Henderson and Demond, 2007). Despite numerous installations, PRBs were considered by Warner and Sorel (2003) an experimental technology because their long-term performance was not well known.

PRB longevity, or the length of time when a PRB is able to intercept the contaminated groundwater and trap the contaminants within, is controlled by reactivity (Vikesland et al., 2003; Roberts et al., 2002; Henderson, 2007) and reduction in permeability (Liang et al., 2003; Phillips et al., 2000; Henderson and Demond, 2007). Some PRBs have not achieved their clean-up goals because of design failure (poor hydraulic characterization and thus incomplete plume capture) or because of operational failure due to declining reactivity or loss of hydraulic conductivity of the reactive medium. Three PRBs seem to have suffered this sort of operational failure, one in Monticello, Utah, and two in Denmark (Henderson, 2007).

1.3 Zero valent iron and pumice granular mixtures as reactive media

ZVI has shown its ability to treat, with a high removal efficiency, contaminants of different nature like organic and inorganic contaminants and represents the most used reactive medium. In aqueous environment ZVI is naturally oxidized by water and compounds dissolved in it with the consequent formation of iron corrosion products that are considered one of the main cause of permeability reduction over time. In addition, data gathered from ZVI PRBs installed in a variety of geochemical environments have shown that, the major effect of inorganic constituents on the technology involves the formation of mineral precipitates on the iron surface that can clog the PRB. In particular, calcium carbonate, iron carbonate, iron hydroxide, and iron sulfide precipitates may form in the medium as the pH of the groundwater increases in response to corrosion of the iron metal. Currently research into prevention of performance loss is an on-going area of research (ITRC, 2011).

In particular in order to avoid the possible clogging of the reactive medium and the consequent bypass of the contaminated plume, through more permeable zones, in some application ZVI was mixed with an inert material (e.g. sand).

An innovative reactive medium, having the objective to prevent permeability loss and also to optimize the use of ZVI, sometimes very expensive, is constituted by granular mixtures of ZVI and Pumice proposed for the first time by Moraci et al. (2008). This thesis gathers a series of laboratory studies carried out in order to evaluate the suitability of this new reactive medium in field applications.

1.4 Thesis objectives

In light of previous Ph. D. studies (Rigano, 2008; Suraci, 2011) the objective of this thesis was to study the efficiency of a reactive medium constituted by either ZVI or by mixtures of ZVI and pumice in term of both removal efficiency against heavy metals, in particular copper (Cu) nickel (Ni) and zinc (Zn), and preservation of permeability. To determine the suitability of the candidate PRB material two methods were used: the batch tests and the column tests. The first test is a quick and simple method generally applied to select the appropriate reactive medium among a wide range of candidate materials. The more time consuming column test provides important information about the behaviour of PRB materials in conditions that more closely approximate those in a reactive barrier system. Column tests represent, at present, the only tool used to determine the design parameters of a PRB.

The objective of batch test was to study the reactivity of granular ZVI/Pumice mixtures in different weight ratio (10:90, 30:70, 50:50, 100:0) in the simultaneous presence of nickel and copper at two different concentrations (5 - 50 mg/l for nickel and 50 – 500 mg/l for copper). Batch test using mono-contaminated solutions were also carried out and used as benchmark.

The column tests were carried out using either pure ZVI or a ZVI/pumice granular mixture with a 30:70 weight ratio. Column tests were performed under different flow rates and contaminant concentration conditions, using single metal solutions, in order to study the following aspects:

1. The effect of initial nickel concentration;
2. The effect of flow rate, using solutions contaminated by nickel or copper;
3. The acceleration of column tests by means of higher flow rate or higher contaminant concentration respect to in situ conditions.

The column tests were also performed using individual and combined solutions of Nickel, Copper and Zinc in order to study the following aspects:

- Phenomena of mutual interaction and/or competition among contaminants.

The results of each test were analysed in term of contaminant removal and variation of hydraulic conductivity.

2. PERMEABLE REACTIVE BARRIERS

2.1 Definition and Applications

A PRB is an in situ technology for groundwater remediation alternative to the traditional Pump and Treat technology.

According to the definition provided by the EPA in the year 1998 Permeable Reactive Barriers are:

> "*An emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals downgradient of the barrier.*"

It simply consists of a permeable wall filled with a reactive medium and installed perpendicularly to groundwater flow in order to intercept the contaminated plume and degrade or trap the contaminants within (Figure 2-1).

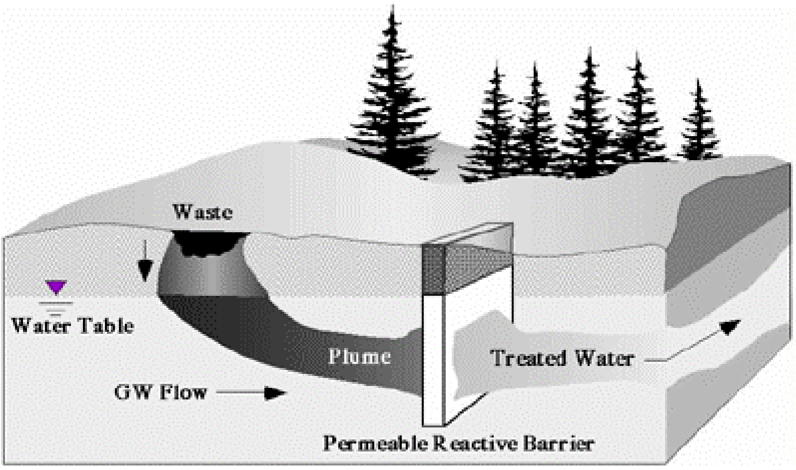


Figure 2-1 Permeable reactive barrier

As already mentioned the most used reactive medium is the zero valent iron, its use has evolved from innovative to accepted standard practice for the containment and treatment of a variety of groundwater contaminants. Worldwide, there have been nearly 120 applications of iron-based PRBs, 83 of which are considered full scale. In the United States, there have been more than 90 applications of iron-based PRBs, 67 of which are full scale (ITRC, 2005).

With the initial success of PRBs, their use has become more widespread. Since the first implementation, the PRB has remained an evolving technology with new and innovative reactive materials introduced to treat different contaminants as well as innovative construction methods, now considering all types of reactive media more than 200 PRB systems have been installed (ITRC, 2011).

In Table 2-1are summarized the reactive media, the treatable contaminants and their use in field applications (PEREBAR, 2000)

Table 2-1 Data on permeable reactive barrier applications

reactive material	treatable contaminants	field applications
Fe^0 Iron sponge Pd, Ni, Cu coated Fe Fe^0, O Fe^0, sand, concrete mixture Zero-valent iron pellets	Organic materials: 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, tetrachloromethane, trichloromethane, dichloromethane, tetrachloroethylene, trichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,1-dichloroethene, vinyl chloride, 1,2-dichloropropane, Freon 113, benzene, toluene, ethylbenzene, hexachlorobutadiene, 1,2-dibromoethane, N-nitrosodimethylamine Inorganic materials: Cr, Ni, Pb, U, Tc, Fe, Mn, Se, Cu, Co, Cd, Zn, SO4, NO3, PO4, As, Hg	Full scale • Aircraft Maintenance Facility, OR • Caldwell Trucking, NJ Federal Highway Administration (FHA) Facility, Lakewood, CO • Former Dry cleaning Site, Rheine, Westphalia, Germany • Former Manufacturing Site, Fairfield, NJ • Industrial Site, Belfast, Northern Ireland • Industrial Site, Coffeyville, KS Industrial Site, NY • Industrial Site, SC • Intersil Semiconductor Site, Sunnyvale, CA • Kansas City Plant, Kansas City, MO • Lowry Air Force Base, CO • U.S. Coast Guard Support Center, Elizabeth City, NC • Y-12 Site, Oak Ridge National Laboratory, TN • Fry Canyon Site, UT Pilot Scale • Area 5, Dover Air Force Base (AFB), DE • Borden Aquifer, Ontario, Canada • Cape Canaveral Air Station, FL • Massachusetts Military Reservation CS-10 Plume, Falmouth, MA • Moffett Federal Airfield, Mountain View, CA • Savannah River Site TNX Area, Aiken, SC • SGL Printed Circuits, Wayne, NJ • Somersworth Sanitary Landfill, NH • U.S. Naval Air Station, Alameda, CA • X-625 Groundwater Treatment Facility, Portsmouth Gaseous Diffusion Plant, Piketon,OH
Organic carbon containing materials: leaf, peat, sewage sludge, manure, sawdust, wood waste, composted leaf mulch, pine mulch, pine bark	NO_3, SO_4, Cd, Pb, Co, Cu, Ni, Zn	Full Scale • Nickel Rim Mine Site, Sudbury, Ontario, Canada Pilot scale • Public School, Langton, Ontario, Canada

Limestone, hydrated lime	Cr, U, As, Mo, PO_4, Se	Full Scale • Tonolli Superfund Site, Nesquehoning, PA Pilot scale • Public School, Langton, Ontario, Canada
Phosphates	U, As, Mo	Full scale • Fry Canyon Site, UT
Ferrous sulfate	Cr, U, As, Mo	
Natural zeolites: clinoptilolite, mordenite Surfactant modified zeolite (SMZ)	Sr, Ba, Cr, PCE	Full-scale • LEAP Permeable Barrier Demonstration Facility, Portland, OR
Iron oxide, Basic oxygen furnace oxide (BOF), amorphous ferric oxide (AFO)	U, As, PO_4, Sr	Full scale • Fry Canyon Site, UT • Y-12 Site, Oak Ridge National Laboratory, TN
Activated alumina	As, PO_4, Sr	
Organic polymers: Cyclophane I, II	Halogenated hydrocarbons (e.g. chloroform) aromatic compounds (e.g. benzene)	
Sodium dithionite	Cr	Pilot scale • 100D Area, Hanford Site, WA
Activated carbon	Alpha-hexachlorobenzenes (BHC), beta-BHC, DDD, DDT, xylene, ethylbenzene, lindane, methyl parathion	Full scale • Marzone Inc./Chevron Chemical Company, Tifton, GA
Microorganisms: G. matallireducens, A. putrefaciens	Tertiary butyl ether (MTBE), U, Ag, Cd, Co, Cu, Fe, Ni, Pb, Zn	Full Scale • Nickel Rim Mine Site, Sudbury, Ontario, Canada

In Italy there is a pilot scale PRB located near the city of Torino. It is a ZVI PRB designed to remediate a contaminated plume containing chlorinated hydrocarbons (Di Molfetta and Sethi, 2005).

2.2 Installation

The main possible configurations for a PRB are:

- continuous barriers
- funnel and gate barriers

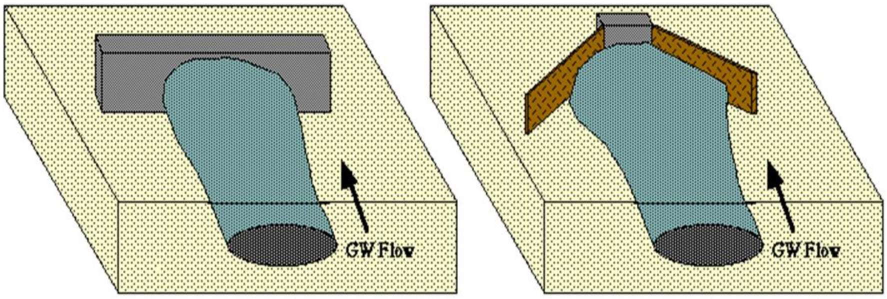


Figure 2-2 Main configuration for PRBs systems: “continuous barriers” and “funnel and gate barriers”

The continuous barrier completely intercepts the plume flow path with the reactive medium whereas, the funnel-and-gate configuration, directs the contaminant plume to a “gate”, containing the reactive medium, through impermeable walls or “funnel” (sheet pilings, slurry walls, etc.). The length of funnels must be significantly longer than the plume width in order to assure complete capture of the contaminants. Typically, the ratio of the length of the funnel to length of the gate is less than six (Day et al., 1999). Due to the funnels, the funnel-and-gate design has a greater impact on altering the ground-water flow than a continuous PRB does.

Typical dimensions of PRBs are 2 to 50 m (perpendicular to the flow direction), <1 to 5 m wide (parallel to the flow direction), and <1 to 10 m deep (RTDF 2001). PRBs have also been installed to greater depths using non-excavation techniques, such as hydraulic fracturing, deep soil mixing (Gavaskar, 1999), or *in situ* redox manipulation (ISRM). This latter creates a reactive zone by reducing iron(III) oxides to iron(II) through the injection of a reducing agent such as sodium dithionate (Fruchter, 2002).

GeoSiphon and GeoFlow Cells (International Patent Application filed December 19, 1997 by Westinghouse Savannah River Company) are innovative alternatives to current groundwater treatment technology. GeoSiphon cells are similar to the funnel and gate concept, except that a siphon is used to increase groundwater flow. The upgradient edge of the siphon is placed in the contaminated plume while the downgradient end can be placed in the subsurface, a surface water body, or the ground surface. GeoSiphon cells work by connecting a large diameter well to a siphon, which accelerates the flow rate between points of a natural head difference. The system is still passive, and the increased flow reduces instances of clogging due to mineral precipitates. The same types of reactive media adopted in conventional PBRs can be used (Bronstein, 2005). The world's first GeoSiphon Cell was installed at the Savannah River Site (SRS) TNX facility in July 1997, for the treatment of trichloroethylene and carbon tetrachloride contaminated groundwater (Phifer et al., 1999).

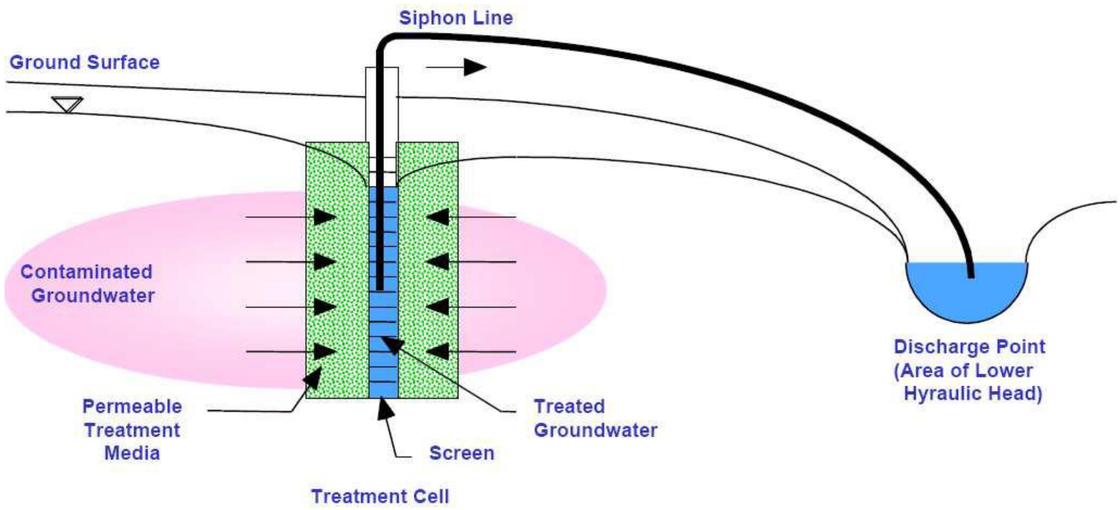


Figure 2-3 GeoSiphon configuration

PRB-like systems may also be installed above ground as *ex situ* systems. Examples of this type of installations are the Portsmouth Groundwater Treatment Facility in Piketon, OH (Korte et al., 1997) and the Uranium Mill Tailings Remedial Action Site in Durango, CO (Morrison et al., 2002). At such installations, the flow of contaminated water is still natural: groundwater is collected in trenches and directed to above-ground containers filled with reactive material that are located below the hydraulic grade line. Although there is no pumping, and the system is thus not active, the fact that the reactive material is installed in a closed container makes these systems very different in practice. In this case the removal and replacement of reactive medium is facilitated. Indeed, the hydraulic conductivity loss observed in these systems is often much greater than that seen in the field (Henderson and Demond, 2007) probably because of the presence of dissolved oxygen.

A new funnel and gate process called panel-drain® was recently developed by the Soletanche-Bachy (Figure 2-4). These panel-drains are composed of several removable cartridges (1 to 3) which are filled by a reactive granular medium and which can be connected in series or in parallel according to the site conditions. As a result, monitoring actions and maintenance operations are facilitated (Courcelles et al., 2008a) .

The selection of the appropriate configuration is primarily dictated by the ability of the PRB to capture the full contaminant plume with a minimal disruption to the natural groundwater flow regime. Numerical groundwater and/or contaminant transport modelling may be required to assess the effects of the selected design configuration (Mountjoy et al., 2003).

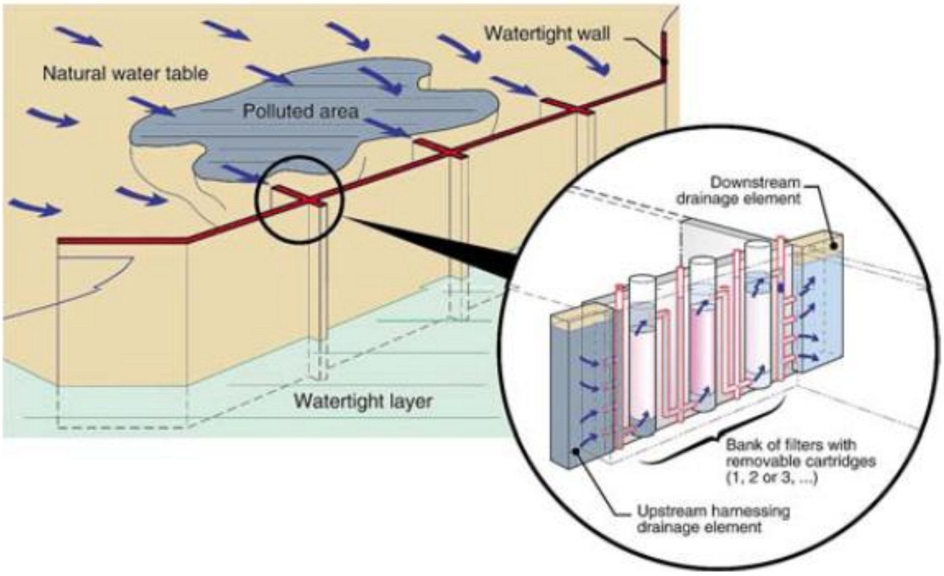


Figure 2-4 Panel-drain principle (Soletanche-Bachy's patent)

2.3 PRB design

The primary goal of any PRB design is to ensure the targeted portion of the contaminant plume is intercepted for treatment and that contaminant flow beneath, around, or above the treatment system does not occur. The second goal is to ensure that the dimensions of a PRB are adequate to achieve the contact time between contaminants and reactive medium needed for the reduction of contaminant concentrations to acceptable levels. Therefore, understanding the site-specific hydrogeology, contaminant and reactive medium properties are critical to the design and construction of a PRB (ITRC, 2011).

The overall methodology for the application of a PRB at a given site is shown in Figure 2-5.

PRB design involves the following steps (Gavaskar et al., 2000):

- Preliminary assessment
- Site characterization
- Reactive media selection
- Treatability testing
- Modelling and engineering design
- Selection of a suitable construction method
- Monitoring plan preparation
- Economic evaluation.

2.3.1 Preliminary assessment

The preliminary assessment is conducted to evaluate the technical and economic suitability of a given site for PRB application. A Preliminary Technical Assessment has the objective to specify the factors that need to be considered to determine the suitability of a site for PRB application. These factors are (Gavaskar et al., 2000):

- Contaminant Type
- Plume Size and Distribution
- Aquifer Depth
- Geotechnical Considerations
- Competent Aquitard
- Groundwater Velocity

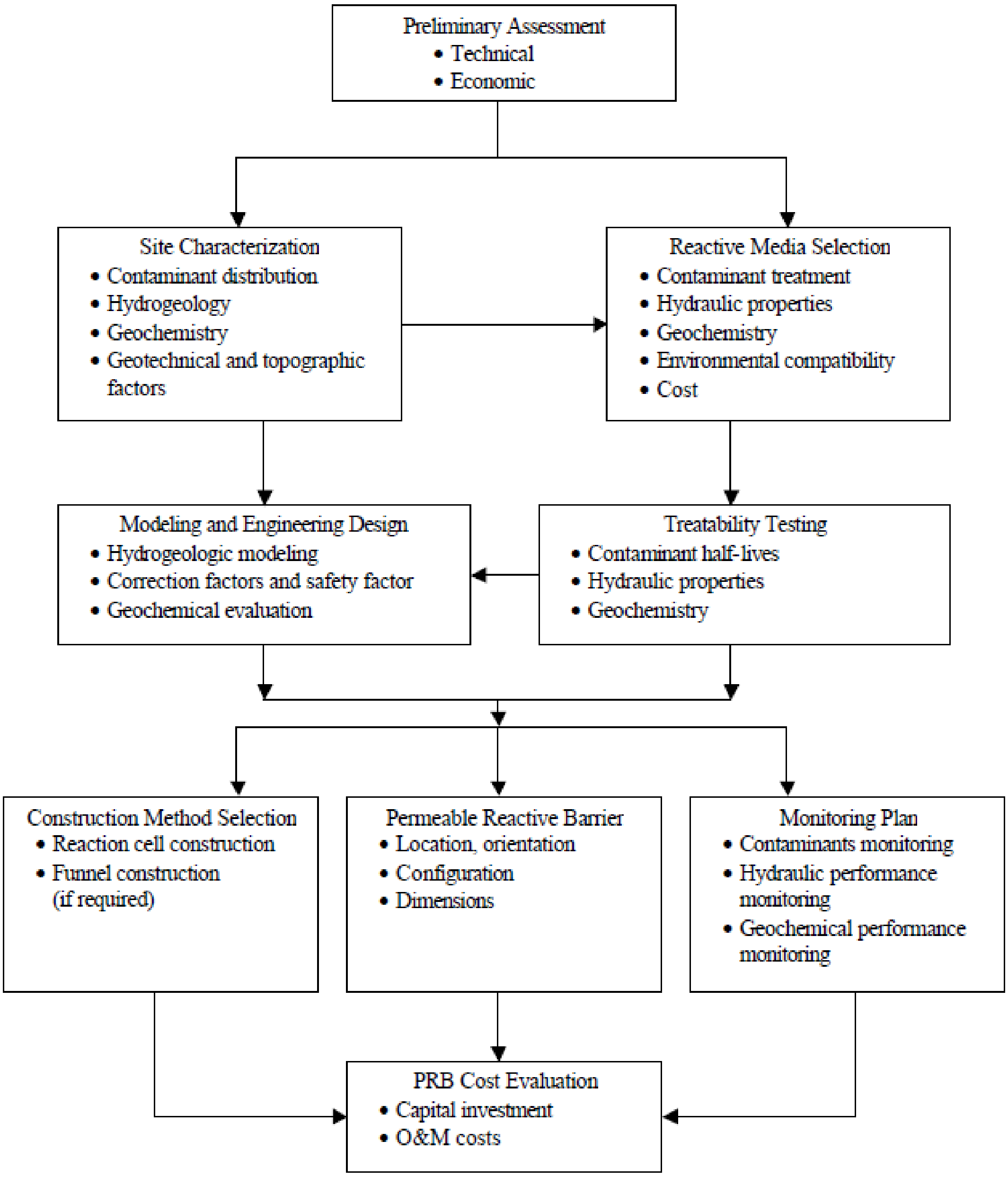


Figure 2-5 Design Methodology for a PRB Application (Gavaskar et al., 2000)

2.3.2 Site Characterization

A site characterization requires the knowledge of the following factors: soil types, depth of water, groundwater flow direction, groundwater velocity, hydraulic conductivity, porosity, depth to confining layer, and dimensions, depth and contaminants concentration of the dissolved plume. Hydrogeological investigations are essential in determining the hydrogeologic properties of the aquifer and may include: water level monitoring using pressure transducers, hydraulic conductivity testing, pump tests and tracer tests. The most significant data to be collected include variations in the depth, thickness, and water levels of different hydrostratigraphic units. This is achieved by drilling and sampling at several locations using conventional drilling or other techniques, such as cone penetrometer testing (CPT) or the use of a Geoprobe. However, at small sites, the traditional monitoring wells are likely to provide more reliable and higher resolution data. The data for hydraulic conductivity, porosity, and water levels are used to determine groundwater velocity at the site (Gupta and Fox, 1999).

2.3.3 Reactive medium selection

The choice among the possible reactive media to be used in PRB constructions is governed by the following considerations (Gavaskar et al., 2000):

- Reactivity: A medium with faster degradation rates is preferred.
- Stability: It is important that the reactive medium is able to maintain its reactivity.
- Availability and Cost. A cheaper medium is preferred over a more expensive medium, especially if any differences in performance are reported to be slight.
- Hydraulic Performance. The particle size of the reactive medium should be sufficient to ensure required hydraulic capture by the barrier. Moreover, the reactive medium should be a filter for the aquifer.
- Environmental Compatibility. The reactive medium should not introduce harmful by-products into the down gradient environment.
- Construction Method. Some innovative construction methods, such as jetting, may require a finer particle size distribution in the reactive medium.

2.3.4 Treatability testing

Treatability testing is carried out to evaluate the performance of the reactive medium with groundwater from a specific site for the following purposes (Gavaskar et al., 2000):

- Screening and selecting a suitable medium for the reactive cell
- Estimating the half- life of the degradation reaction
- Determining the hydraulic properties of the reactive medium
- Evaluating the longevity of the reactive medium.

Treatability testing for the screening and selection of the suitable reactive medium for the reactive cell is accomplished by batch tests. Batch experiments, as it will be better explained in § 4.6, are generally carried out by placing the medium and the contaminated solution in septum-capped vials which are put in rotation for a short period (about one week or less).

Contrary to batch tests column ones can simulate the reactive medium behaviour under flow conditions. As better explained in § 4.7, a column test is generally carried out using a column with multiple sampling ports along its length. The column is packed with the reactive medium and water is circulated in the column from bottom to top. Sampling ports are constituted of syringe needles permanently inserted into the column, with the tip at the centre of the column and allow to withdraw solution samples.

2.3.5 Modelling and engineering design

Barrier dimensions include length (y) perpendicular to groundwater, flow-through thickness, or width (z), and depth (x) (Figure 2-6). The PRB must be long enough to treat the entire width of the plume (dimension perpendicular to groundwater flow). The thickness of the PRB is designed based on the required residence time of the contaminants for treatment and the groundwater flow velocity. The residence time is the contaminant contact time with the reactive medium that must be sufficient to allow contaminant remediation. It depends on the constituent degradation rate, maximum contaminant concentrations, and groundwater flow rate. Regarding the depth of a PRB, if at all possible, the PRB should extend to and be keyed into a competent bedrock layer or aquitard. (ITRC, 2011).

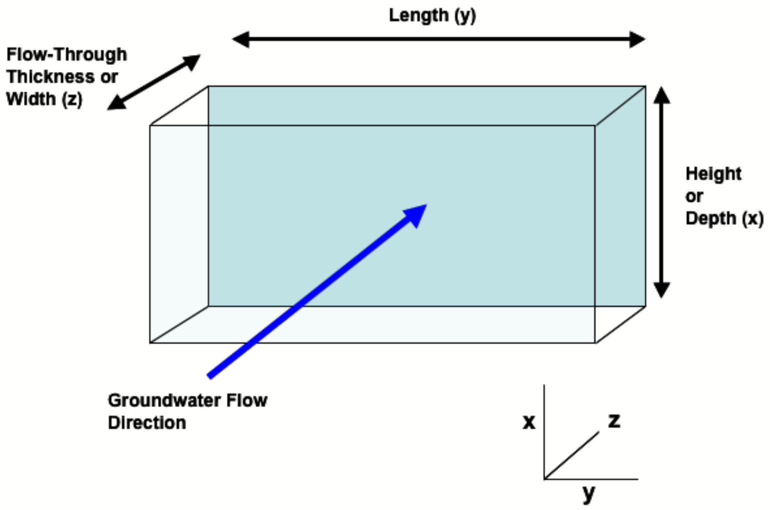


Figure 2-6 Dimensions of a PRB (ITRC, 2011)

2.3.5.1 Reaction Kinetics and Residence Time

In order to evaluate the required PRB flow-through thickness (Figure 2-5), the evaluation of the residence time is necessary and the primary parameters required to estimate this parameter are the rate at which the contaminant(s) are degraded and the maximum contaminant concentrations. Determining degradation rates that can be achieved using a PRB is challenging since each site is unique with widely variable conditions (ITRC, 2011).

A first attempt to evaluate degradation rates has been made for the degradation of Chlorinated Volatile Organic Compounds (CVOCs) by zero valent iron (Sivavec and Horney, 1995; Gavaskar, 1999). In order to determine the degradation rate constant, CVOC concentrations were plotted as a function of distance through the reactive column. When the flow rate and porosity are known, distances through the column can be converted easily to residence times. It is calculated as the product of the bed void fraction (n) and the reactor volume (V), divided by the liquid flow rate through the bed (Q). A graph of contaminant concentrations (μg/L) versus residence time (in hours) then can be generated. A degradation rate constant, k, can then be calculated assuming a first-order kinetics (eq. 1).

$$C = C_0 e^{-kt} \qquad \text{eq. 1}$$

Where C is the value of contaminant concentration measured at time t. When ln (C/C_0) is plotted against time in hours (Figure 2-7) the slope of the fitted line is the reaction rate k (h^{-1}). The degree of fit can be determined by calculating the correlation coefficient (r^2). The r^2 value indicates how well the pseudo first-order model fits the experimental data.

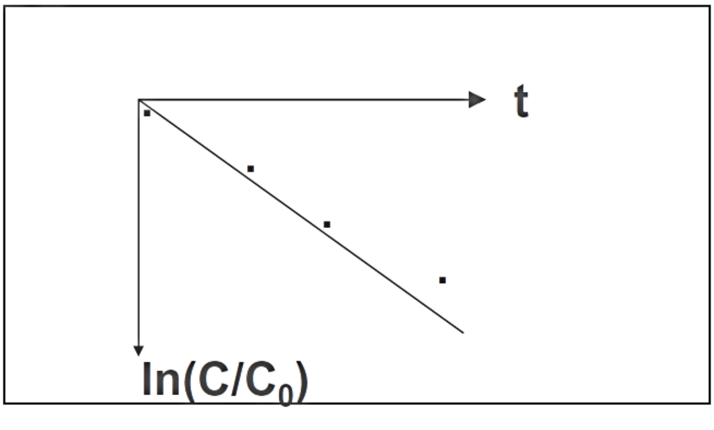


Figure 2-7 ln (C/C_0) plotted against time

Once the rate constant is known, a half- life can be estimated using Equation 2 for each contaminant of interest in the influent. A half- life is the time period required to reduce the concentration of a contaminant by half.

$$t_{1/2} = \frac{log2}{k} = \frac{0,693}{k} \qquad \text{eq. 2}$$

The wall thickness "L" can be determined using the following equation:

$$L = t_{res} \cdot V \cdot FS \qquad \text{eq. 3}$$

and:

$$t_{res} = -\frac{ln^{C_t}/_{C_o}}{k} \qquad \text{eq. 4}$$

Where C_t is the concentration target; C_0 is the concentration at source; t_{res} is the time of residence in the wall; V is the velocity of the water; k is the reaction rate; and FS is the safety factor. The Safety factor reflects uncertainties and fluctuations in parameter values and clearly increases the amount of reactive material employed (Johnson et al., 1996).

Subsequently studies have shown that, the rate of contaminant reduction by iron metal is not only first order in contaminant concentration but that it also appears to be first order with respect to the amount of metal available to serve as reductant. To describe this behaviour, the pseudo-first-order kinetic model used to determine k_{obs} can be expanded to:

$$C = C_0 e^{-k_{obs}t} \qquad \text{eq. 5}$$

$$k_{obs} = k_{sa}\rho_a \qquad \text{eq. 6}$$

$$\rho_a = a_s\rho_m \qquad \text{eq. 7}$$

where k_{SA} is the specific reaction rate constant (L $h^{-1}m^{-2}$), a_s is the specific surface area of Fe^0 (m^2 g^{-1}), ρ_m is the mass concentration of Fe^0 (g L^{-1} of solution), ρ_a is the surface area concentration of Fe^0 (m^2 L^{-1} of solution). Since $k_{obs}=k_{SA}\rho_a$ where $\rho_a=a_s\rho_m$, the model suggests that straight-line plots should be obtained from k_{obs} versus ρ_a, a_s, or ρ_m (Johnson et al., 1996).

Reduction rates characterized in these terms should be independent of the mass and specific surface area of the metal and the volume of the reaction system.

It should be noted that the first-order kinetics are mostly reported for initial reaction rates and that the rates are increasingly deviated from the first-order kinetics with increasing time (Melitas and Farrell, 2002; Ponder et al., 2000).

The previous design formula for calculate wall thickness (eq. 3), attempts to have the target concentration at the exit of the barrier and not at the point of compliance. The formula also does not account for dispersion. Neglecting dispersion, a commonly used assumption in PRB analysis, can lead to non-conservative designs (Amine, 2008; Rabideau et al., 2005).

2.3.5.2 PRB modelling considerations

PRB design requires the modelling of three aspects: hydrogeologic, geochemical and economic conditions. These aspects can be modelled by a single combined model or by coupled independent models. An hydrogeologic model attempts to quantify the effect of a particular barrier design on the groundwater system. It should be able to handle site complexities (e.g. site heterogeneities, streams, drains, tunnels, and wells) that may cause preferential flow pathways, groundwater sources, or groundwater sinks. A geochemical model attempts to predict the concentrations of dissolved species in groundwater based on assumed chemical reactions. The geochemical model needs to include both solute transport (including advection and dispersion) and the necessary chemical reactions. The economic model is generally the most straightforward as its objective is to calculate the present value of the construction and operational costs for a particular PRB design (Painter, 2005).

2.3.5.3 Hydrogeologic modelling

Hydrogeologic modelling allows to provide an estimate of the capture zone for a given PRB design. A "capture zone" refers to the three-dimensional region that contributes the ground water extracted by one or more wells or drains. The modelled capture zone then helps the designer to calculate the appropriate flow-through thickness and the required permeability of the reactive medium (ITCR, 2011).

Hydrogeologic models are used in order to incorporate the site-specific hydrogeology conditions into the design of the permeable barriers. Hydrogeologic models can be used at several stages of the permeable barrier technology implementation, including the initial feasibility assessment, the site selection, design optimization, design of the performance monitoring network, and the longevity assessment.

MODFLOW, in conjunction with particle tracking with codes such as MODPATH, are the codes most commonly used to simulate the permeable barriers technology (Gupta and Fox, 1999).

2.3.5.4 Geochemical models

Geochemical calculations and modelling can be used to evaluate the rates of contaminants removal by reactive medium and to investigate potential precipitation impacts to the reactive medium. Results of the transformation of inorganic constituents of column tests can be used as inputs into such modelling efforts (ITCR, 2011).

Geochemical models can simulate physical transport processes coupled to the geochemical processes. Since these models simulate simultaneous transport and reaction of several chemical components, they are commonly referred to as multi-component reactive transport models (Kumar, 2006).

The modelling of equilibrium geochemistry of natural waters is a well-established field. Computer models for solving equilibrium geochemistry problems that have been widely used include WATEQ , MICROQL, MINEQL, MINTEQA2, PHREEQE, PHREEQC and EQ3/6 and its derivatives (Kumar, 2006).

2.3.6 Selection of a suitable construction method

Various construction techniques have been used to emplace PRB's. These include: conventional excavation and back filling, trenching machines, tremie tubes or mandrels, deep soil mixing, high-pressure jetting in conjunction with vertical hydraulic fracturing and reactant sand sealing. Among these methods, conventional trenching and backfilling has most commonly been applied to continuous PBRs, while sheet-pile driving and slurry walls have been most commonly used for the impermeable section of funnel and gate PRBs (Mountjoy et al., 2003).

Slurry walls are constructed by first excavating a trench under a head of liquid slurry. The slurry, which is usually a mixture of bentonite and water, helps maintaining the integrity of the trench by forming a filter cake over the face of the wall. As a trench is excavated, it is quickly refilled with a mixture of cement and bentonite or a selected soil-bentonite backfill. The more common slurry walls constructed are the soil-bentonite and the cement-bentonite slurry walls. Another, but less common, type is the plastic concrete slurry wall (Gavaskar et al., 1997).

The selection of the construction technique mainly depends on site characteristics (Gavaskar, 1999), e.g.:

- depth (the most important factor): increasing depth requires more specialized equipment, longer construction times and is accompanied by higher costs;
- geotechnical considerations: soil/rock strength and presence of obstacles;
- soil excavation: handling and disposal of (contaminated) soil;
- health and safety during construction (entry of personnel into excavations).

Conventional trenching techniques include unsupported excavation and supported excavation. The first is the simplest and least expensive installation, but the soil must have sufficient cohesion to remain open until the trench is backfilled with the reactive material. Temporary support methods such as trench boxes have been used in case of supported excavation. These two conventional techniques can be used to install PRBs to maximum depths of 8 m below ground surface (ITRC, 2011).

For example a funnel and gate system PRB, constructed in Sunnyvale (Ca.) in 1995, was installed using the conventional trench and fill method. Installation proceeded by driving sheet piling to the appropriate depth and then excavating the sheet piling cell. The treatment wall was keyed into slurry walls (Figure 2-8).

Figure 2-8 Intersil Site, Sunnyvale, Ca., 1995 - Trench Gate (backhoe) and slurry funnel wall

Another funnel-and-gate PRB was installed at Dover Air Force Base (Battelle, 1997). The construction method for this system is shown in Figure 2-9. Each gate consisted of an 2.5 m diameter caisson containing reactive media, and pre- and post-treatment zone sands. Funnel walls were constructed using sheet piling up to a depth of about 13 m.

Figure 2-9 Dover Air Force Base, Dover, De., 1997- Sheet pile funnel & caisson gates

Continuous-trenching machines allow simultaneous excavation and backfilling without an open trench. Trenchers are available to install treatment zones from 0.5 to 0.9 m in width and to depths of 11 m (ITRC, 2011).

The first application of the continuous PRB configuration in a full-scale system to treat a combined inorganic and organic plume was at Elizabeth City, North Carolina. A continuous PRB composed of zero-valent iron was installed in June, 1996 using a trencher that was capable of installing the granular iron to a depth of 7 m (Figure 2-10).

Figure 2-10 Coast Guard site, Elizabeth City, NC 1996- Continuous wall using continuous trencher

An injected PRB is made drilling a series of boreholes and then injecting the reactive media under pressure, often using a carrier fluid (e.g., high-pressure gas, water, or other solution) to carry the media into the subsurface. In particular hydraulic fracturing is the injection of a slurry solution at a pressure that exceeds the combined lithostatic pressure and cohesive strength of the formation. The method uses high initial pumping pressures to initiate fracturing of the contaminated strata, followed by subsequent injection at pressures as low as 1 psi (~7 KPa)for the reactive media solution to fill the induced fractures (ITRC, 2011).

Alternative construction techniques include vertical hydrofracturing that is the injection of iron in vertical planes using a biodegradable gel and an enzyme to biodegrade the gel.

This technique was applied at Caldwell Trucking site, New Jersey (Figure 2-11). The fracturing fluid used at the Caldwell trucking site, consisted of potable water, guar gum, a borax cross-linker (to link iron to the gel), pH buffer, an enzyme breaker (to break down starch in the guar after injection), and a fine-sand propant (Hocking, 1998).

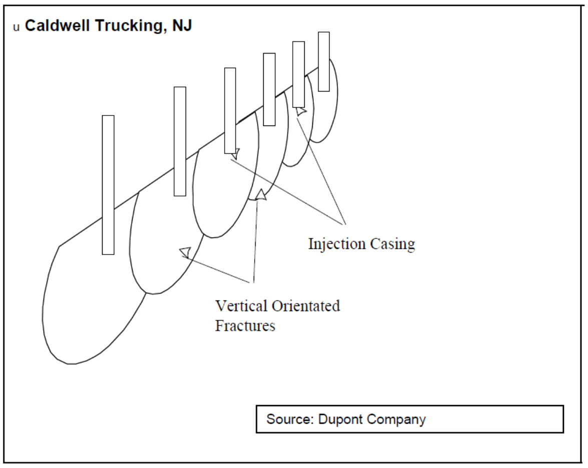


Figure 2-11 Caldwell Trucking site, NJ - fractures filled with iron slurry

In the technique of Deep soil mixing, large in situ soil mixing augers with diameters of 3 m add reactive media such as ZVI in reactive columns to a depth of over 15 m below ground surface (Figure 2-12). Deep soil mixing can also be used to install permeable funnels in funnel-and-gate configurations. This technique uses one to three large augers (1–2.5 m in diameter) with mixing paddles along the treatment zone. Fine iron is added as the augers penetrate the ground and mix the iron with the subsurface materials. The iron can also be introduced in biodegradable slurry. This method generates minimal spoils and reduces costs associated with the removal of contaminated soils. However, equipment mobilization costs may make this method prohibitive, especially at small sites (ITCR, 2011).

.

Figure 2-12 Iron slurry fed through hollow stem augers

During jetting or jet grouting, grout or slurry is injected into the subsurface at high pressures. A triple-rod injection system delivers a high-pressure mixture of granular iron, guar gum, air and/or water. The rods are advanced to the design depth of the PRB, and the injection begins. The grout and slurry are continually injected as the rods are pulled toward the surface, creating a column or panel of reactive medium (ITRC, 2011).

The PRB using the double-rod columnar jetting process was constructed in June, 1999 at Travis Air Force Base, Ca. (Figure 2-13).

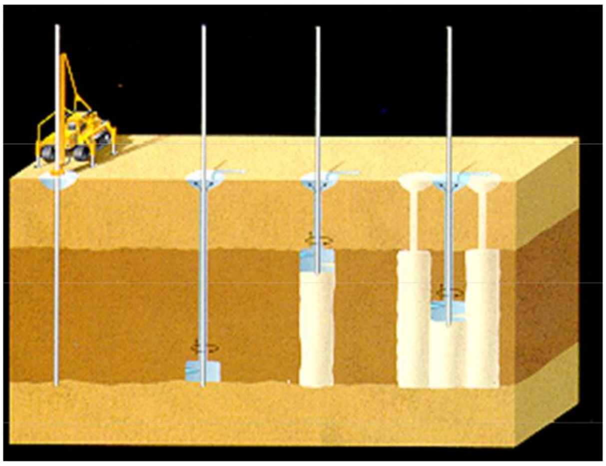


Figure 2-13 Travis Air Force Base, Ca. 1999 - Travis Air Force Base, Ca. 1999

Using tremie tubes or mandrels, an H-beam or mandrel (hollow steel shaft) with a special shoe at its base is driven into the subsurface, creating a void space. As the beam/mandrel is pulled out of the ground, reactive medium or a slurry/grout-containing reactive medium is injected into the created void through a nozzle (tremie tube) connected to the bottom of the beam (ITRC, 2011). This technique was tested at Cape Canaveral Air station FL (Figure 2-14) to investigate its suitability for installing a PRB (Gavaskar et al., 2000).

Figure 2-14 Pilot Test at Cape Canaveral, Fl. 1997 - granular iron tremied into hole

In August 1999, at the Pease Air Force Base of New Hampshire, a PRB was installed using a biopolymer slurry technique where the total VOC concentration exceeded 1,000 mg/L and the site was contaminated with TCE and subproducts (Figure 2-15). A total of 487 tons of sand and 359 tons of granular iron were installed in a trench. In order to improve hydraulic conductivity of the barrier, 75 l of enzyme were injected into the barrier through a 15 cm PVC flushing well to help in the degradation of biopolymeyuyr. The contaminants were degraded inside the wall (Amine, 2008).

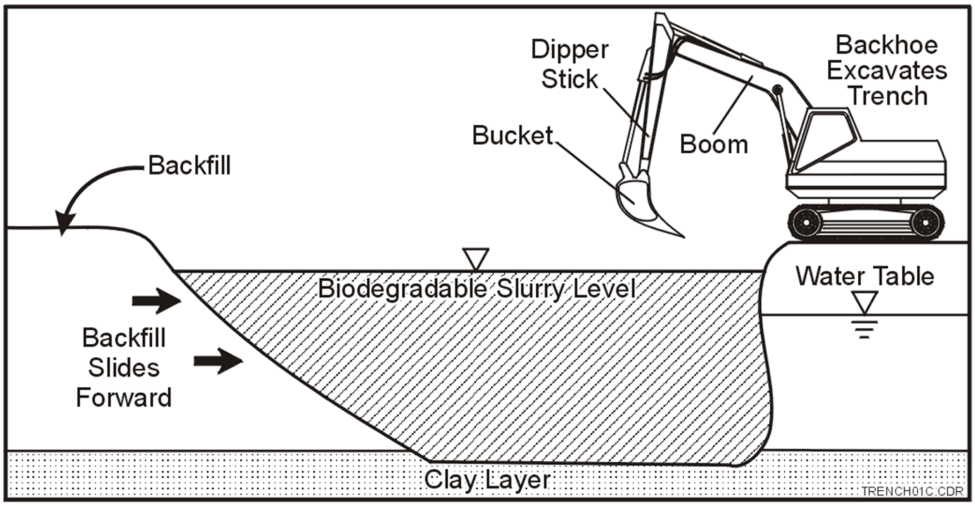


Figure 2-15 Bioslurry - Pease Airforce Base, NH, 1999

The excavation of the PRB installed in Italy was performed using a crawler crane equipped with an hydraulic grab and supported by guar gum slurry (Figure 2-16). The trench was backfilled with iron and the biopolymer degraded using enzymes (Di Molfetta and Sethi, 2005).

Figure 2-16 Torino, 2004 - Crawler crane equipped and hydraulic grab used in the excavation.

PRBs are often capped with materials such as clay, clay and a geotextile or pavement, depending on the activities at the ground surface (Kiilerich et al., 2000). But it is necessary to consider that PRB capping is an impediment to migration of gases generated by chemical reactions between the reactive medium and the contaminated plume (e.g. hydrogen gas generated by ZVI oxidation in anaerobic conditions).

Table 2-2 summarizes the PRB designs, hydrogeological and contaminant conditions that have been applied in the UK (Smith et al., 2003).

Table 2-2 Application of PRBs in the UK (Smith et al., 2003)

Location	Contaminants	Geology	PRB design	Reagent	Depth of PRB (m)
Belfast	Chlorinated ethenes	Sand & Gravel over Sherwood Sandstone	Funnel & Gate (using vertical flow reactor)	Fe^0	8
Portadown	PAH, ammonium	Sand & Gravel over glacial till	Funnel & Gate	Sand bioreactor / air injection & GAC	5
West Yorkshire	Chlorinated ethenes	Sand & gravel over Coal Measures	Funnel & Gate (2 gates)	Fe^0	10
Essex	BTEX, chlorinated ethenes, other organics	Sand & Gravel over London Clay	Funnel & Gate (multiple gates)	GAC	7
Northumberland	Iron, aluminium, pH, sulphate	Coal Measures	Continuous	Manure / compost / limestone bioreactor	<5
Wiltshire	Chlorinated ethenes, BTEX	Sand & Gravel over Chalk	Continuous	GAC	<5
Devon	PAH, cyanide	Sand & Gravel over Permian Breccia	Funnel & Gate	Multi-sequence biological reactor	7
Worcestershire	Chlorinated ethenes (principally TCE)	Sand & Gravel over Mercia Mudstone	Funnel & Gate	Fe^0	6
Greater Manchester	Chlorinated alkanes, organosulphur compounds	Sand & Gravel over glacial till	Funnel & Gate	Fe^0	5
Northumberland	PAH	Fluvial silts	Funnel & Gate	GAC	<5

2.3.7 Monitoring plan preparation

Once the PRB has been designed and constructed, the system must be monitored as long as the plume exists. The primary objective of contaminant monitoring is to verify that the groundwater quality downstream of the PRB is in compliance with the target cleanup objectives agreed to by site managers and regulators. In other words, monitoring seeks to establish that the plume is being adequately captured and treated (Gavaskar et al., 2000).

2.3.8 Economic evaluation

Key variables that affect PRB economics are the length of time that a given installed reactive medium will retain its reactive and hydraulic performance and, consequently, the type and frequency of the maintenance required to replace and/or regenerate the reactive medium (Gavaskar et al., 2000).

An economic evaluation of a PRB scheme needs to take account of (Roehl, 2005):

- Expenditure on the site investigation;
- Cost of preliminary and feasibility studies;
- Planning and engineering;

- Construction costs;
- Costs of reactive materials (including any recovery, replacement and disposal costs);
- Maintenance;
- Monitoring (to verify long- term performance and demonstrate remediation success).

3. ZVI AND ZVI/PUMICE MIXTURES USED AS REACTIVE MEDIA

3.1 Zero valent iron

As already mentioned, the most used reactive medium in installed PRBs is the Zero Valent Iron. Zero-valent (or elemental/ native) iron (Fe^0) can be found under some specific environmental and geological conditions (e.g. in some mafic and ultramafic rocks and in meteorites). It is, however, rarely formed at the Earth's surface due to the high reactivity of elemental iron. In fact, Fe is found in the environment dominantly in two valence states the relatively water-soluble Fe(II) (ferrous iron) and the highly water-insoluble Fe(III) (ferric iron) (Cundy et al., 2008).

The ZVI used for PRB applications generally is recycled scrap iron coming from the manufacture of automotive parts (e.g., engine motors, brake drums, etc.). Another rare source of ZVI is molten iron, which is then granulated with high-pressure water jets. The granulated iron is sieved to a specified grain size (ITRC, 2011).

ZVI used in PRB applications should have a high fraction of iron metal (> 90%), low carbon content (< 3%), and nonhazardous levels of leachable trace metal impurities. It must be free of any surface coatings (oils or grease) that may inhibit its reactivity. The surface area of ZVI particles is very important because reactions occur at the iron/water interface. Reaction rates generally increase as the surface area of the ZVI particles increases. For PRBs constructed using excavation-based methods, the grain size range typically used is 2.0 – 0.25 mm, which provides an average hydraulic conductivity of about 10^{-2} cm/sec. Typically, the surface area of this coarse ZVI has a range of 0.5 – 1.5 m^2/g.

In recent years the interest to emplace finer-grained fractions of 1.0 mm or less (microscale ZVI) and nanoscale iron particles using injection-based techniques is growing. Thanks to the higher surface area, nanoscale iron particles have a high reactivity but relatively short life. They are best suited to remediation of source zones, where they can degrade a relatively large quantity of contaminant, especially volatile organic compounds (VOCs), in a short period of time (ITRC, 2011). Microscale and nonoscale iron particles can be dispersed in a viscous suspension and injected directly into the ground at the source of contamination (Di Molfetta and Sethi, 2006).

Zero-valent iron (ZVI) has been used successfully to remediate groundwater contaminated by chlorinated organics (Gillham et al., 1994; Cundy et al., 2008) and metals (Cantrell et al., 1995; Blowes and Ptacek, 1992; Blowes et al., 2000) contamination through PRB. Fe^0 used in filtration systems or Fe beds have also been proven efficient for safe drinking water provision at household level (Noubactep, 2010).

3.1.1 Zero valent iron corrosion processes

The reaction involved in ZVI /H_2O systems are reassumed in Table 3-1 (Noubactep, 2009c). ZVI can be oxidized from the oxidized form of the contaminant (Ox) which reduction yields a corresponding reduced form (Red) (Table 3-1 eq.1). ZVI is also oxidized by water, that, as solvent, is present in stoichiometric abundance, under anoxic (Table 3-1 eq.2) and oxic (Table 3-1 eq. 3) conditions. Fe^{II} species resulting from eq. 1 to eq. 3 may be oxidized to Fe^{III} species by molecular O_2 or other available oxidants (Ox1: contaminant, MnO_2) (eqs. 4 and 5). Under anoxic conditions, H_2 from eq. 2 may reduce the contaminant (eq. 6). The process of H_2O reduction by ZVI increases the pH of the system, promoting the formation of iron hydroxides (eqs. 7 and 8). Iron hydroxides are then transformed through dehydration and recrystallisation to various iron oxides depending on the geochemical conditions (eq. 9). Iron (hydr)oxides are good adsorbent for several contaminants (eq. 10). During their precipitation, iron hydroxides may sequestrate contaminant in their matrix (eq. 11). (Noubactep, 2009c).

Table 3-1 Reactions involved in Fe^0/H_2O systems

Reactions	
$Fe^0+Ox \leftrightarrow Fe^{2+} + Red$	(1)
$Fe^0+H_2O \leftrightarrow Fe^{2+}+H_2+2OH^-$	(2)
$Fe^0+O_2+2H_2O \leftrightarrow 2Fe^{2+}+4OH^-$	(3)
$Fe_{aq}^{II}+Ox_1 \leftrightarrow Fe_{aq}^{III}+ Red_1$	(4)
$Fe_{(s)}^{II}+Ox_1 \leftrightarrow Fe_{(s)}^{III} + Red_1$	(5)
$H_2+OH \leftrightarrow H^+ + Red$	(6)
$Fe^{2+}+2OH^- \leftrightarrow Fe(OH)_2$	(7)
$Fe^{2+}+3OH^- \leftrightarrow Fe(OH)_3$	(8)
$Fe(OH)_2, Fe(OH)_3 \leftrightarrow FeOOH, Fe_2O_3,Fe_3O_4$	(9)
$Fe_xO_y+Ox \leftrightarrow Fe_xO_y\text{-}OH$	(10)
$Ox+nFe_x(OH)_y^{(3x-y)} \leftrightarrow Ox[Fe_x(OH)_y^{(3x-y)}]_n$	(11)

The oxidation of ZVI by a contaminant (eq. 3) is a spontaneous electrochemical process that involves the reduction of a more electropositive (noble) species by more electronegative (sacrificial) metals. This reaction is possible as standard redox potential of the oxidant specie is higher than the one of ZVI ($E_{FeII/Fe}$= -0,44 V). Beside ZVI and H_2, Fe^{II} adsorbed on a mineral surface (structural Fe^{II} or $Fe_{(s)}^{II}$) has been reported to be a very strong reducing agent, suggesting that, dissolved Fe^{II} and structural Fe^{II} are further contaminant reducing agents in ZVI /H_2O systems (Noubactep, 2009c).

The electrode potentials of the redox couples of iron (−0.44V for Fe^{II}/Fe^{0} and −0.35 to −0.65V for $Fe_{(s)\ III}/Fe_{(s)I}$) suggests that, from a pure thermodynamic perspective, in some circumstances ($E < -0.44$ V), contaminant reduction by Fe^{II} might be more favourable than reduction by electrons from ZVI.

The presence of iron hydroxides and other ferrous and ferric oxides (eqs. 7 - 8) cause passivation of the ZVI surface. Furthermore as an oxide layer is formed on the ZVI surface, a contaminant should migrate across the film to adsorb on the ZVI surface and undergo reduction, alternatively, the oxide layer should be electronic conductive to warrant electron transfer (Noubactep, 2009c).

Among iron oxides formed during iron corrosion process (eq. 9) magnetite (Fe_3O_4), which is known to form due to anaerobic ZVI corrosion, passivates the ZVI surface (Forukawa et al., 2002)

3.1.2 Contaminants removal mechanisms by ZVI

In the last two decades metallic iron has been extensively used in different remediation schemes to effectively remove a wide variety of inorganic and organic contaminants.

As previously mentioned, ZVI can be oxidized from the oxidized form of contaminant (Ox) which reduction yields a corresponding reduced form (Red). Furthermore reduction process can generally involve direct reduction at the surface of ZVI or catalytic reduction through Fe^{II} at the surface of corrosion products (Noubactep, 2009c).

The reduction can be explained based on the standard oxidation-reduction potentials of the metal ions. As presented in Table 3-2, for metals such as zinc and cadmium, that have E_0 more negative or very close to that of ZVI, there is no reduction of the metal ions on the surface and the removal mechanisms are only sorption or complex formation. For metals having a E_0 far more positive than ZVI, such as copper, silver, mercury, the removal mechanism is predominantly reduction, precipitation, cementation and pore size exclusion.

Table 3-2 Standard Electrode Potentials at 25°C

	$E^0(V)$	
Barium (Ba)	$Ba^{2+} + 2\,e^- \leftrightarrow Ba$	-2.90
Zinc (Zn)	$Zn^{2+} + 2\,e^- \leftrightarrow Zn$	-0.76
Iron (Fe)	$Fe^{2+} + 2\,e^- \leftrightarrow Fe$	-0.41
Cadmium (Cd)	$Cd^{2+} + 2\,e^- \leftrightarrow Cd$	-0.40
Nickel (Ni)	$Ni^{2+} + 2\,e^- \leftrightarrow Ni$	-0.24
Lead (Pb)	$Pb^{2+} + 2\,e^- \leftrightarrow Pb$	-0.13
Copper (Cu)	$Cu^{2+} + 2\,e^- \leftrightarrow Cu$	0.34
Silver (Ag)	$Ag^{+} + e^- \leftrightarrow Ag$	0.80
Mercury (Hg)	$Hg^{2+} + 2\,e^- \leftrightarrow Hg$	0.86
Chromium (cr)	$Cr_2O_7^{2-} + 14H^+ + 6e- \leftrightarrow 2Cr^{3+} + 7H_2O$	1.36

Reduction is not in fact the only contaminant removal mechanism, iron corrosion products can in fact play a relevant role in term of contaminant immobilization through adsorption and co-precipitation processes. Freshly precipitated, amorphous Fe oxyhydroxides are known to be particularly effective adsorbents of a range of contaminants (Cundy et al., 2008), due to their high (reactive) specific surface area. Coprecipitation is a mechanism in which corrosion products, during precipitation, may entrap adsorbed contaminants in their mass (Crawford et al. 1993; Sridharan & Lee 1972). Coprecipitation and adsorption are favoured at high pH in accordance with the corrosion processes and in the presence of dissolved oxygen. Reduction and coprecipitation are irreversible process while adsorption is reversible.

Therefore contaminants can be removed at three different possible sites: at the surface of ZVI, within the film of corrosion products and at the surface of corrosion products (Noubactep, 2006).

The effect of iron corrosion products can be beneficial in terms of contaminant removal, but their precipitation on the surface of ZVI, blocks the reactive sites and can decrease the PRB porosity with the consequent bypass of the contaminant plume around the PRB treatment zone.

Li and Zhang in 2008 studied nanoscale ZVI (nZVI) structure before and after the contact with various metals and proposed three possible types of metal uptake on nZVI surface. Figure 3-1 shows the core-shell structure of nZVI suggested by the authors. According to this view only physical sorption occurs for cations having standard reduction potential, E^0, more negative than or close to that of Fe, both sorption and chemical reduction arise for cations having E^0 slightly more positive than that of Fe and only chemical reduction occurs for cations with E^0 substantially higher than that of Fe. There are several studies that focused on the characterization and synthesis mechanisms of nZVI, but further effort is still needed to better clarify its structure.

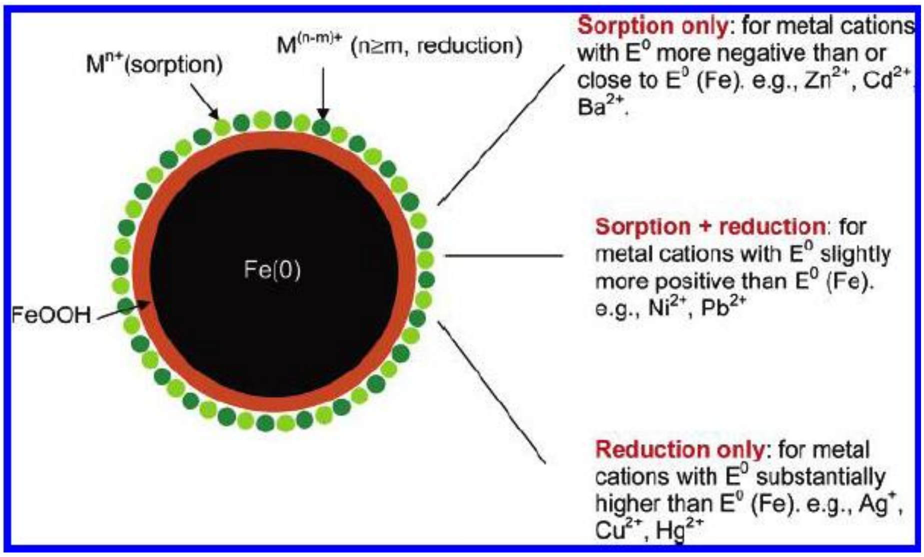


Figure 3-1 A conceptual model for metal removal with nZVI

3.1.3 Long term performance of ZVI-PRB

Due to the variability of geochemical and hydrological site conditions, despite the extensive field iron PRBs applications, there is still much uncertainty in predicting their long-term effectiveness defined as the ability of the reactive medium to remove contaminants and to keep its hydraulic performance over long periods of time.

The long term performance of a PRB depends by different factors as type and concentration of contaminants, removal processes, type and mass of reactive material, hydraulic characteristics of the site (flow velocity) and geochemical characteristics of the ground-water, Eh, pH, composition).

Processes that influence the long-term performance of PRBs are:

- Coatings of the particles surface of the reactive material by precipitation of secondary minerals and corrosion ("rust");
- Clogging of the pore space between the particles by oxidized iron expansion, precipitation of secondary mineral, gas formation (H_2) and biomass production;
- Exhaustion of the reactivity of the reactive medium.

Some field and laboratory investigation have suggested that fouling in PRBs may result in preferential flow and/or blockage of flow (e.g. Sarr, 2001; Kamolpornwijit et al., 2003; Vikesland et al., 2003). Bypass of groundwater flow was for example documented by Morrison et al. (2006) and Li et al. (2005).

Literatures studies have indicated that the possible causes of ZVI barrier hydraulic efficiency reduction are iron expansion, mineral precipitation, accumulation of hydrogen gas released from oxidation of ZVI and microbial activity (Mackenzie et al., 1999; Liang et al., 2000; Bartzas et al., 2006; Henderson and Demond, 2011).

In particular formation of biofilms or oxide layers on the ZVI surface could cover the active redox sites and thus reduce its reactivity and in addition can cause decrease in porosity and permeability (Steefel and Lasaga, 1990; Benner et al., 2000; Gu et al., 2002; Komnitsas et al., 2007).

The porosity reduction of the reactive medium over time is especially due, according to recent research, to the volume of iron corrosion products being higher than that of the original metal. The ratio (η) between the volume of expansive corrosion product and the volume of iron consumed in the corrosion process is called coefficient of volumetric expansion (Carè et al., 2008; Zhao et al., 2011). Generally, the volume of corrosion products (V_{oxide}) is 2.08 to 6.40 times larger than the initial volume of ZVI (V0) ($2.08 < \eta < 6.40$).

The type of the secondary minerals that can precipitate inside the PRB is primarily dependent on the solution chemistry and the prevailing flow conditions. Groundwater normally contains carbonate in various concentrations. An increase in pH, due to effect of iron corrosion, will cause a shift in the carbonate-bicarbonate equilibrium, and thus result in the formation of carbonate mineral precipitates according the following reactions (Mackenzie et al., 1999):

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$$

$$Fe^{2+} + CO_3^{2-} \leftrightarrow FeCO_3(s)$$

$$Ca_2^+ + CO_3^{2-} \leftrightarrow CaCO_3(s)$$

Depending on local geochemical conditions, carbonate-containing minerals, such as iron hydroxy carbonate ($Fe_2(OH)_2CO_3$) (Jeen, et al., 2006) and carbonate green rust ($[Fe_4Fe_2(OH)_{12}][CO3.2H_2O]$) can also form (Bonin et al., 2000).

In many studies, in order to reduce material costs, the prevention of loss of reactivity and reduction of hydraulic conductivity mixing zero-valent iron with sand was proposed. Another solution is to create a pretreatment zone (PTZ) immediately upstream of the PRB containing gravel or sand in certain cases with reactive medium mixed in. Such zone, as suggested in the literature, allows for precipitate formation with minimal permeability reduction, and can therefore reduce potential clogging at the upstream of a PRB (Sarr 2001; Dwyer 2000).

Summarizing, permeability reduction and reactivity decline of Fe^0 PRB is a significant concern regarding long-term performance of iron PRBs. In particular, the reasons for iron reactivity decrease could be due to a reduced number of reactive sites or reduced reactive surface area, or declining rate of electron transfer across progressively thicker or insulating precipitate layers, or a combination of the two. In many studies an attempt to evaluate the long-term performance of iron PRBs was to use quantitative models capable of predicting the relationship between the precipitates with the change of iron reactivity and effectiveness of PRBs (O'Hannesin and Gillham, 1998; Mayer et al., 2001; Liang et al., 2003).

In order to restore the permeability loss due to precipitate formation and possibly to remove the precipitate from the iron to restore its reactivity the following rejuvenation methods can be considered:

- using ultrasound to break up the precipitate;
- using PPT (pressure pulse technology) to break up the precipitate;
- using solid-stem augers to agitate the PRB;
- periodic flushing with nitrate free water to remove nitrates.

No full-scale test to rejuvenate mineralized ZVI has been performed to date (ITCR, 2011).

3.2 ZVI/Pumice granular mixtures

The idea of mixing the ZVI to pumice was introduced for the first time by Moraci et al., 2008. The role of pumice is to scatter the ZVI mass into a greater volume in order to prevent the hydraulic conductivity loss of the barrier due to the expansive nature of ZVI corrosion products. The first laboratory experiments on ZVI/Pumice granular mixtures were carried out by Rigano (2008) and Suraci (2011).

In particular, the ZVI and the ZVI/Pumice granular mixtures at a weight ratio of 50:50 and 30:70, behaviour was tested through column tests, these latter have showed high removal efficiency towards copper and nickel when the initial contaminant concentration was of 50 and 5 mg/l respectively (Rigano, 2008). In these circumstances, column tests results confirmed that, granular mixtures of ZVI and Pumice have a significant remediation capacity for groundwater contaminated by heavy metals, reaching results both in terms of concentration and mass removed at the outlet of the column comparable to those of the columns containing ZVI only. The performance of granular mixtures with 30:70 and 50:50 weight ratio is very similar notwithstanding the higher ZVI content of the latter. For both contaminants the metal was almost completely removed in the first 3 cm of the column for all duration of the tests. This behaviour is due to the mass of ZVI used in the columns that greatly exceeds the amount necessary to remove the mass of contaminant flowing through the column during the test (Moraci et al., 2011).

The effect of the weight ratio between ZVI and Pumice (i.e. 10:90, 30:70 and 50:50) was studied using a contaminated solution of Nickel at initial concentration of 50 – 5 and 0.5 mg/l (also Moraci et al., 2010b). When the lowest values of nickel concentration were used the effect of weight ratio is negligible because the metal is always removed by solution for all duration of the tests. When the highest nickel concentration was used none of the reactive media tested were able to reach the concentration set by Italian Regulation. Although the 50:50 granular mixture has shown a better performance, the 30:70 one gave 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 (Calabrò et al., 2011). It can be stated that the reactivity and, in general the performance of the granular mixture is enhanced if the ZVI/Pumice weight ratio is high, instead a low ZVI/Pumice weight ratio favours a better preservation of hydraulic conductivity. From this study, it can be stated that, the best compromise between reactivity and long term preservation of hydraulic conductivity is probably given by the 30:70 granular mixture (Calabrò et al., 2011).

Three configurations of reactive material (ZVI only, granular mixture of ZVI and pumice, and pumice and ZVI in series) was also studied by Suraci (2008) using nickel and copper solutions at initial concentration of 50 and 500 mg/l respectively. In the configuration in series the pumice was placed downstream of the iron so that the pumice removal capacity could also be analysed. In order to facilitate comparison of the test results, an identical quantity of ZVI (240 g) was used in each column. The same quantity of pumice (560 g) was used in the column loaded with pumice and ZVI in series and in the column loaded with VI/pumice mixture (Moraci and Calabrò, 2010). The configuration of ZVI and pumice to form a mixture has showed a better behaviour both in term of contaminant removal and preservation of hydraulic conductivity than the other two configurations.

3.3 Hydraulic performance of PRBs

As discussed above, the precipitation of solids has been observed in numerous PRBs. Literature shows different attempts to relate this solid accumulation to the porosity reduction of a PRB (Henderson, 2004; Li et al., 2006; Komnitsas et al., 2006; Courcelles et al., 2008a; Courcelles et al., 2008b; O et al., 2009).

The hydraulic conductivity of a saturated porous medium is defined by Darcy's Law (Jury and Horton, 2004) which states that the volumetric flow rate per unit area (q) is proportional to the gradient of the hydraulic head:

$$q = -k\nabla J \qquad \text{eq. 8}$$

the Darcy velocity q is the volumetric flux Q/A_{bulk}; k is the hydraulic conductivity and J is the total head, the energy per unit weight of water relative to the reference state. The Darcy velocity is not a true velocity, the average velocity $\bar{v}$ is higher because the area for flow is less than the bulk area, as described by porosity, n, i.e. $\bar{v} = q/n$ (Charbeneau, 2000).

The hydraulic conductivity, k, is related to the intrinsic permeability K of the porous matrix as follow (Nutting, 1930):

$$k = \frac{K\rho g}{\mu} \qquad \text{eq. 9}$$

where ρ is the density, g is the gravitational constant and μ is the dynamic viscosity of the liquid. The intrinsic permeability (dims. L^2) depends solely on the properties of the solid matrix.

Purely theoretical formulas for K are obtained from theoretical derivation of Darcy's law. Usually, such formulas include numerical coefficients which have to be determined empirically. An example is the Kozeny-Carman equation (Bear, 1972):

$$K = C_0 \frac{n^3}{(1-n)^2 M_S^2} \qquad \text{eq. 10}$$

Where Ms is the specific surface area of the solid matrix (defined per unit volume of solid) and C_0 is a coefficient for which Carman (1973) suggested the value of 1/5.

Based on the above equation, a loss of porosity, due to precipitation in the case of the porous media in a PRB, can be equated with a loss of permeability.

An attempt to modelling a permeability loss due only to solids was carried out by Henderson (2006) using the following Kozeny-Carman relationship:

$$K = \frac{D_e^2}{180} \cdot \frac{n^3}{(1-n)^2} \qquad \text{eq. 11}$$

The above equation is limited to conditions in which the flow is laminar, and it does not work well for irregular particles, in which the measured and calculated specific surface areas are not similar. However, the Kozeny-Carman equation has been shown to predict, within a factor of 3, the hydraulic conductivity of homogenized soils with $10^{-1} < K < 10^{-11}$ m/s (Chapuis and Aubertin, 2003).

An attempt to evaluate porosity reductions that occurs in PRBs containing granular ZVI as result of precipitation of minerals in the pore spaces, was also conducted by Li et al. (2006) using a code program which combine MODFLOW and RT3D to simulate flow and reactive transport in PRB and includes a geochemical algorithm developed for simulating geochemical reaction that occurs in PRBs. The model was validated trough two field PRB present in literature. Reductions in hydraulic conductivity of the ZVI were estimated using the Kozeny-Carmen equation (Bear 1972) assuming a specific surface constant. Only mineral precipitates were assumed to contribute to the change in porosity, the effects of gas evolution and accumulation and biological matter were ignored.

The authors Courcelles et al. (2008b) used a model based on Kozeny-Carman's equation but taking into account the specific surface evolution as a function of the size of the particles forming the permeable medium (Le Gallo et al.,1998):

$$K = \frac{n^3}{\tau(1-n)^2 \cdot S^2} \qquad \text{eq. 12}$$

With τ the tortuosity and S the specific surface (m^2/m^3).

The numerical model developed by Courcelles et al. (2008b) is close to Fair-Hatch model, which gives the permeability as a function of the volumetric fraction of the minerals composing the permeable material and their respective diameter (Le Gallo et al.,1998):

$$K = \frac{n^3}{\tau(1-n)^2 \cdot \left(\sum_{i=1}^{n_m} \frac{\varphi_i}{r_i}\right)^2} \qquad \text{eq. 13}$$

Whereφ_i is the volumetric fraction of mineral i, r_i is the radius of spheres and Nm the Number of minerals. For the precipitates a spherical shape was considered and the specific surface of a filter element was calculated from the diameter of each of the solid species and their respective number. The authors found this model seems to be able to predict clogging by precipitates of PRB filters.

4. MATERIALS AND METHODS USED IN THE RESEARCH

4.1 Introduction

The materials used in this research are Fe^0 and Pumice. The two materials and different mixtures of them were tested through batch and column tests in order to evaluate their applicability as reactive media in PRB. In particular, their efficiency to treat groundwater contaminated by heavy metals (i.e. Ni, Cu and Zn) was evaluated.

4.2 Zero valent iron

The zero-valent iron used is marketed as FERBLAST RI 850/3.5, distributed by Pometon S.P.A., Mestre Italy. It is mainly composed of ZVI (>99.74%), with limited impurities consisting of manganese (0.26%) and traces of oxygen, sulphur and carbon. The average diameter was about 0.500 mm (500 µm). Grain size distribution of ZVI is represented in Figure 4-1.

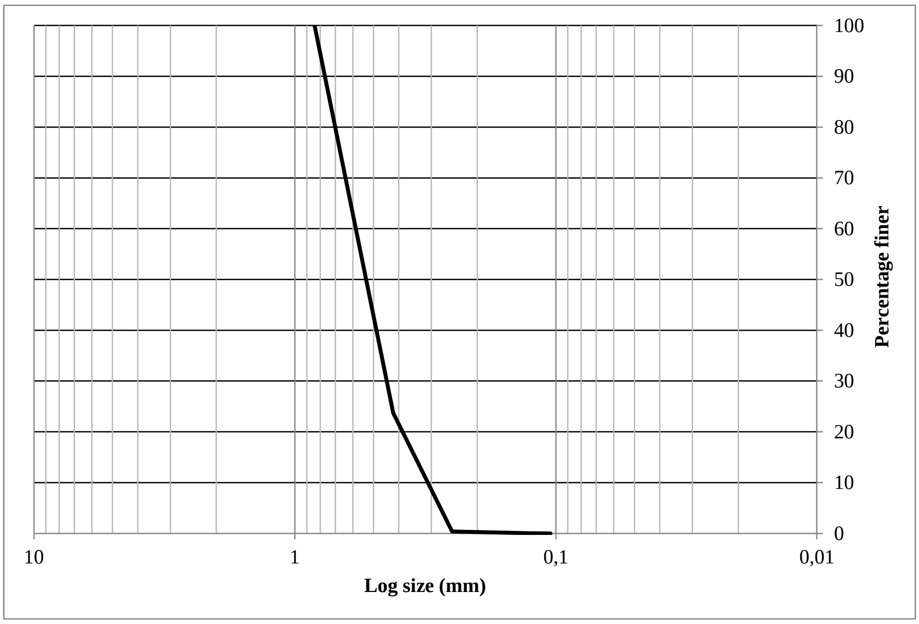


Figure 4-1 Grain size distribution of zero valent iron

4.3 Pumice

Pumice is a volcanic rock with a spongy, vitreous structure, characterized by a high internal porosity due to the expansion of magmatic gases during the effusion process by which it was generated.

The largest pumice producer in the world are Turkey, Italy, Greece, China and Iran. There are two kinds of pumice: acidic pumice and basic pumice. Acidic pumice is the most common pumice type in the world. It is therefore used in the construction industry, particularly in the production of light-weight brick and concrete elements that have thermal/acoustic insulation capabilities. Many studies have been conducted to determine possible usage areas of pumice as well as the above-mentioned traditional usage area. In this scope, many researchers have studied the use of natural and/or modified pumice as an adsorbent for organic (i.e. phenol, textile dyes) and inorganic (various heavy metals and radioactive elements) water pollutants (Ersoy et al., 2010).

The pumice used in this research comes from the quarries of Lipari (Aeolian Islands, Sicily – Italy); it is a natural complex silicate (Pumex Spa, 2008) constituted mainly by silica (SiO_2 – 71.75%) and by oxides of various elements (e.g. Al_2O_3 – 12.33%, K_2O – 4.47%, Na_2O – 3.59%, Fe_2O_3 – 1.98%, MgO – 0.12%, TiO_2 – 0.11%, MnO – 0.07%, FeO – 0.02%) (Pumex, 2008).

Pumice is generally considered chemically inert, since it is insoluble both in water and in acids or bases, except hydrofluoric acid (HF).

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

$$> SiOH + Me^{2+} \leftrightarrow (> SiO^{-} — Me^{2+})^{+} + H^{+} \qquad \text{eq. 14}$$

where > represents the pumice surface.

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

The average diameter of pumice used in the research was about of 0.300 mm (300µm); it was the available fraction closest to ZVI in grain size distribution. Grain size distribution of pumice is represented in Figure 4-2.

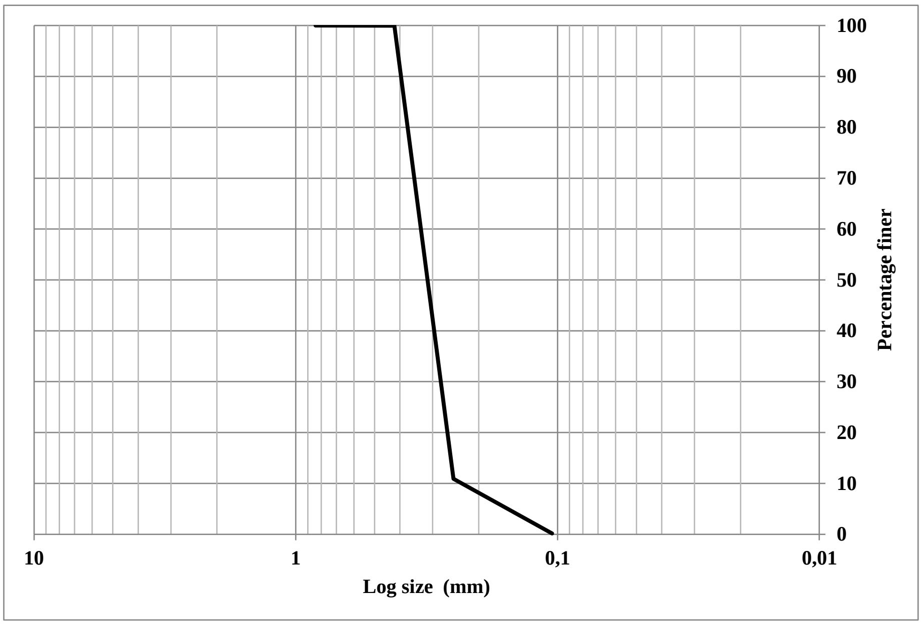


Figure 4-2 Grain size distribution of pumice

4.4 ZVI/Pumice mixture w.r. 30:70

The reactive medium, tested in the research through column tests, is a granular mixture of the ZVI and Pumice described in the previous paragraphs. The two materials were mixed with a weight ratio 30:70 the grain size distribution of the mixture is represented in Figure 4-3.

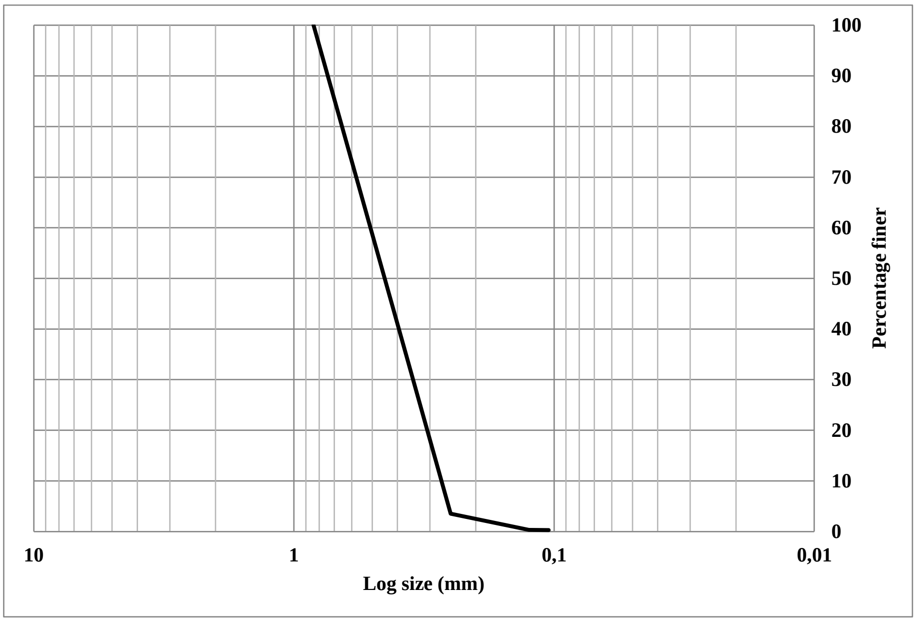


Figure 4-3 Grain size distribution of the mixture ZVI/Pumice (w.r. 30:70)

4.5 Chemicals and solutions

The contaminants tested in the research are heavy metals: Copper (Cu), Nickel (Ni) and Zinc (Zn). The term "heavy-metals" refers to a large group of chemical elements of the Periodic Table having densities greater than 6 g/cm^3. The differences among heavy metals are associated with their atomic weights and their varying degrees of toxicity for organisms. Heavy-metals are non-biodegradable. In both aquatic and terrestrial systems they circulate in various chemical forms. For example, they are dissolved in water in form of ions or they associate with solid phases such as oxides, clay minerals, organic matter, etc. (Ambrosini, 2004).

The reasons why Cu, Ni and Zn were tested are because they belong to the most problematic chemical elements found at hazardous waste sites in the United States. Frequently, contaminated groundwater from industry or mining activities contains these heavy metals. Another reason is because these metals can be measured easily in laboratory with analytical techniques, in particular with spectrophotometry.

For the experiments, the contaminated aqueous solutions were obtained by dissolving the regent in distilled water. The reagents, obtained from Sigma-Aldrich, are:

- Copper(II) nitrate hydrate (purity 99.999);
- Nickel(II) nitrate hexahydrate (purity 99.999);
- Zinc(II) nitrate hexahydrate (purity 99.000).

4.6 Batch test apparatus

Batch tests are usually carried out in order to select the reactive medium able to remove a given contaminant. The test is performed putting in contact the reactive medium with the contaminated solution, with a preset liquid-solid ratio, in septum-capped vials with no headspace, and putting them in rotation. When liquid samples are drawn from the vial for analysis, the vial can be sacrificed or alternatively nitrogen can be added to fill up the headspace created. Normally the first option was used in this research. The apparatus used in this research is an end over end rotating stirrer Stuart Scientific Rotator Drive STR/4.1 (Figure 4-4).

Figure 4-4 Batch test apparatus

4.7 Column test apparatus

Column tests can give information towards the design of a PRB and indications on how an in situ PRB will perform. Laboratory scale polymethyl methacrylate (Plexiglas) columns were used in this research. Column tests were carried out in up-flow mode. The influent solution was pumped, through the column, from a single PE bottle at a known flow rate using a precision peristaltic pump. In order to carried out column tests at different flow rate simultaneously in some cases two multichannel peristaltic pump (Ismatec, ISM930) were used, respectively 4 and 12 channels available (Figure 4-5).

Figure 4-5 Peristaltic pumps equipped with 4 channels (left) and 12 channels (right)

The columns were equipped with sampling ports located at different distances from the inlet. In each port a needle is inserted with the tip on the axis of the column. Sampling ports allow to determine changes in contaminant concentration and other parameters (e.g. pH) along the column length and at the outlet (Figure 4-6).

Figure 4-6 Sampling port

Columns have an internal diameter of 5 cm and height equal to 50 or 100 cm respectively. Sampling ports are located at distance of 1.5, 3, 5, 8, 13, 18, 23, 28, 33, 38, 53.3 cm from inlet for the column having an height 50 cm. The distance from inlet of the last sampling port (the effluent sampling port) is referred at 50 cm of reactive medium height. Sampling ports for the column height 100 cm are located at distance of 3, 8, 18, 28, 38, 58, 78, 100 cm from inlet. A schematic diagram and a photo of column test apparatus are represented in
Figure 4-7 and Figure 4-8 respectively.

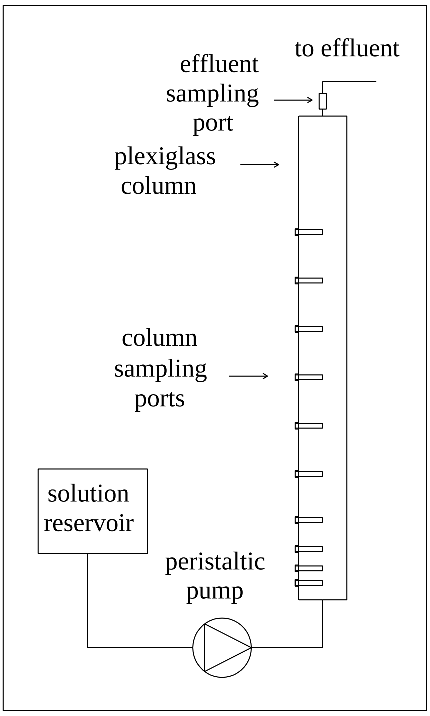


Figure 4-7 Schematic diagram of column test apparatus

Figure 4-8 Photo of column test apparatus

In order to ensure that the column tests are sufficiently representative to be used to determine PRB design parameters, the physical, chemical and hydraulic conditions should be kept as similar as possible to those in situ. In this study, the reactive media used are identical to those used in actual PRBs in terms of physical and chemical characteristics such as composition and grain size distribution. Therefore, during column test design attention must be concentrated on the hydraulic conditions. The two main issues are possible channelling and wall effects associated with the use of column tests and the accurate reproduction of in situ hydrodynamic conditions. The prevention of channelling and wall effects ensures that a small column of reactive medium behaves similarly to an indefinitely large actual PRB and in particular that the behaviour of the reactive medium is not influenced by the proximity of the column surface. According to Badruzzaman and Westerhoff 2005, these effects may be avoided if the ratio between the column diameter (D) and the mean particle size (d) is greater than 50. In the experiments presented in this paper this ratio was about 130 for ZVI alone and about 150 for the ZVI/pumice mixture. Reproduction of hydrodynamic conditions is somewhat more complex in practice. According to relevant reports (Crittenden et al., 1991), the best way to comply with this criterion is to keep the experimental flow rates and Peclet numbers as similar as possible to the field values.

Table 4-1shows a survey of column dimensions and flow rates adopted in literature.

Table 4-1 Variability of the operational conditions for column experiments as illustrated by the dimension of the column (H, D), the nature of contaminants (X), the nature of reactive medium (RM), the flow rate (Q). D is the internal diameter of the column and H its length.

Ref.	X	H (cm)	D (cm)	RM	Q (ml/min)	Reason for Q choice
Roh et al. 2000	U235, Tc95m, TCE	35	2	ZVI	2, 6.2	Not specified
Baciocchi et al. 2003	TCE	100	5	ZVI	0.5	Typical field cond.
Kamolpornwijit et al. 2003	NO3-, metals	90	15	ZVI	1.5	Typical field cond.
Kamolpornwijit et al. 2003	NO3-, metals	90	15	ZVI	33.5	Accelerated cond.
Wantanaphong et al. 2006	AMD*	50	4.4	ZEO, CS**	0.35, 2.08	Not specified
Bartzas et al. 2006	AMD	45	5	ZVI	0.23	Typical field cond.
Bartzas et al. 2006	AMD	45	5	ZVI	1.14	Accelerated cond.
Komnitsas et al. 2007	Cu	45	5	ZVI	0.23	Typical field cond.
Komnitsas et al. 2007	Cu	45	5	ZVI	1.14	Accelerated cond.
Moraci and Calabrò 2010	Ni, Cu	50	5	ZVI/Pumice	0.5	Not specified
Prasad et al. 2011	CrVI	20-60	2.5	ZVI	18.5 – 55.5	Not specified
Wanner et al. 2011	CrVI	100	6	ZVI	2.55	Specific site cond.
* AMD = Acidic mine drainage (synthetic) ** ZEO = clinoptilolite and CS = calcified seaweed						

Most often in the papers present in scientific literature the reason for selecting a determinate flow rate is not specified, in other cases the chosen value is presented as representative of “typical field conditions” while only in one case (Wanner et al., 2011) the chosen value is representative of a real site. As can be verified in Henderson and Demond 2007, where the average flow rates registered in sixteen real PRBs sites are reported, the range in field conditions is quite large (0.015 - 5.7 m/d) also if the median value of registered flow rate is of 0.25 m/d and the analysis of the data seems to show that lower flow rates are more frequent than higher ones in sites where real PRBs are installed.

4.8 Atomic Absorption Spectrophotometry

Measurements of aqueous concentrations of contaminants were carried out by Atomic Absorption Spectrophotometry (AAS - Shimadzu AA – 6701F – method) using conventional Standard Methods (APHA 2005) (Figure 4-9).

AAS determines the presence of metals in liquid samples and also measures the concentrations of metals in the samples. Typical concentrations range in the low mg/L range.

The technique requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on Beer-Lambert Law. In short, in their elemental form, metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interest is aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. Through Beer-Lambert Law the absorbance is converted in concentration value.

Figure 4-9 Atomic Absorption Spectrophotometry

4.9 Material characterization

The microstructure of used Fe^0 and pumice was characterized using mercury intrusion porosimetry (MIP) measurements and by scanning electron microscopy (SEM) observations at the Université Paris-Est, Laboratoire Navier, Ecole des Ponts (I am grateful to Dr. Sabine Caré for her help). The observations enable a characterization of the morphology of both materials and the pumice inner pore structure.

4.9.1 SEM

A scanning electron microscope (SEM) is an electron microscope that gives information about sample's surface topography, composition, and other properties such as electrical conductivity. A SEM images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The signals produced by SEM result from interactions of the electron beam with atoms at or near the surface of the sample and include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors.

SEM images, detailing the microstructure of the Fe^0 and pumice particle, are shown in Figure 4-10, during SEM observations secondary (Hitachi, type: s3400N) observations secondary electron mode was used. Pumice particles were coated with carbon. These observations show that the Fe^0 and pumice particles are irregular. It can be observed that the pumice particles are porous with oval shaped and fibrous cavities (or pores). The diameter of these cavities is lower than about 40 µm.

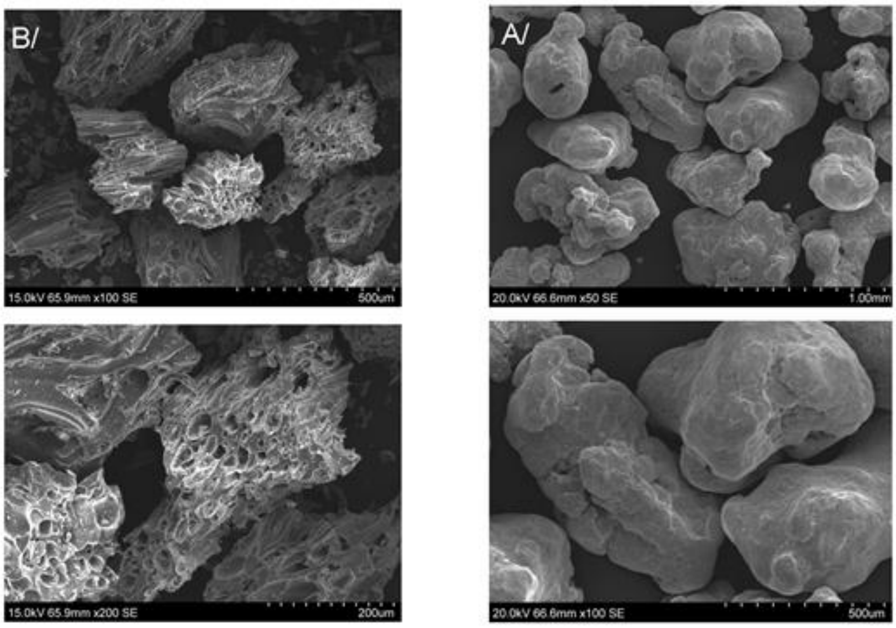


Figure 4-10 SEM images of the ZVI particles (A) and of the pumice particles (B)

4.9.2 MIP

MIP consists of injecting mercury into a porous material. The in-pore invasion process is supposed to be governed by the Washburn-Laplace equation in which the size of intruded pore accesses assimilated to cylindrical pores are inversely proportional to the applied pressure according to Eq. 15:

$$P = -\frac{2\gamma\cos\theta}{R_P} \qquad \text{eq. 15}$$

where P is the mercury injection pressure (Pa), γ is the surface tension of mercury (485 dyn.cm^{-1}), θ is the contact angle between solid and mercury ($\theta = 130°$) and R_p is the pore access radius for cylindrical pores (m). MIP measurements have been carried out using a Micromeritics instrument apparatus type. The instrument is capable of a minimum intruding pressure of 3.4 kPa and a maximum pressure of 227 MPa, so that the pore radius ranges from 2.7 nm to 180 μm.

For pumice particles the measured pore data allow determining the apparent specific weight ρ_{as} (defined as the ratio of the mass and the apparent volume of the pumice particles) and the specific weight ρ_s (defines as the ratio of the mass and the volume of the solid phase of the pumice particles). The results for ZVI and for the pumice are shown in Table 4-2.

Table 4-2 MIP results

	Fe^0	Pumice
Specific weight ρ_s (g/cm^3)	7.87	1.92
Apparent specific weight ρ_{as} (g/cm^3)	7.87	1.14

5. TEST PARAMETERS AND EXPERIMENTAL PROGRAM

5.1 Definitions

Column tests parameters can be referred to the test conditions (reactive medium, contaminant solution and flow rate), to the reactive medium (volume occupied by the reactive medium, porosity and pore volume) and to both (residence time and number of pore volume).

Porosity of the columns was calculated through eq. 16 from the bulk density and particle density of the reactive material used in the experiments:

$$n = 1 - \frac{\rho_b}{\rho_s} \qquad \text{eq. 16}$$

Where ρ_b is the bulk density (g cm^{-3}) which is the ratio between the weight of the medium present in the column (P) and the volume of the column (V), ρ_s is the particle density (g cm^{-3}) of the column medium.

In the case of mixtures the porosity was calculated as follows:

$$n = \frac{V_v}{V_t} = 1 - \frac{\frac{P_{pom}}{\rho_{pom}} + \frac{P_{ZVI}}{\rho_{ZVI}}}{V_t} \qquad \text{eq. 17}$$

Where V_v is the void volume, V_t is the volume of the column occupied by the reactive medium, P_{pom} and P_{ZVI} are the weight of Pumice and ZVI respectively present in the column, ρ_{ZVI} is the ZVI particle density (ρ_s), ρ_{pom} can be referred to the pumice particle density (ρ_s) or to the apparent specific weight ρ_{as}, in the first and latter case the inter-particular porosity (n) and the total porosity (n_t) (included intra-particular porosity of the pumice) can be respectively calculated.

The pore volume (eq. 18) is the volume occupied by the water.

$$PV = n \cdot V_t \qquad \text{eq. 18}$$

The residence time is calculated through equation 19.

$$t_{res} = \frac{PV}{Q} \qquad \text{eq. 19}$$

The number of Pore Volume ($N_{pore\ volume}$) flowed in the column at the time “t” is calculated through equation 20.

$$N_{pore\ volume} = \frac{t}{t_{res}} \quad \text{eq. 20}$$

5.2 Interpretation of column tests

In order to analyze the reactivity of the medium, column tests results are generally represented plotting the normalized concentration of the contaminant $C/C_{0,}$ where C is the effluent concentration and C_0 is the influent concentration, as function of experimental duration at different sampling ports (breakthrough curve).

In order to characterize the capability of tested systems for contaminant removal, the specific removal (SR) and the specific removal related to ZVI only (SR_{ZVI}) were calculated using Eq. 21 and Eq. 22.

$$SR = \frac{m_{rem}}{m_{rea.med.}} \cdot 100 \quad \text{eq. 21}$$

$$SR = \frac{m_{rem}}{m_{ZVI}} \cdot 100 \quad \text{eq. 22}$$

where m_{rem} is the mass of removed contaminant, $m_{reac.med}$ is the mass of reactive medium present in the column (either ZVI or granular mixture) and m_{ZVI} the mass of ZVI present in the column. The removal efficiency is calculated as:

$$E = \frac{m_{rem}}{m_{im}} \cdot 100 \quad \text{eq. 23}$$

where m_{in} is the mass of contaminant flowed into the column.

5.3 Column tests experimental program

In Table 5-1 are listed the experimental program and parameters of column tests performed during the experimental research.

Table 5-1: Column tests program

Reactive Medium	Pumice [g]	ZVI [g]	Cont./Conc. [mg/L]	Flow rate (mL/min)	n (%)	PV [cm^3]	T_{res} [h]
Mix.ZVI/Pum.	560	240	Ni 8	2.5	45	404	2.7
Mix.ZVI/Pum.	560	240	Ni 40	2.5	45	404	2.7
Mix.ZVI/Pum.	560	240	Ni 95	2.5	45	404	2.7
Mix.ZVI/Pum.	560	240	Ni 40	0.5	45	404	13.4
Mix.ZVI/Pum.	560	240	Ni 40	0.1	45	404	67
ZVI	-	1680	Ni 8	2.5	47.7	195	1.3
ZVI	-	1680	Ni 40	2.5	47.7	195	1.3
ZVI	-	1680	Ni 95	2.5	47.7	195	1.3
ZVI	-	240	Ni 40	0.5	47.7	28	0.9
ZVI	-	1680	Ni 40	0.1	47.7	195	32
Mix.ZVI/Pum.	560	240	Cu 500	0.1	45	404	67
Mix.ZVI/Pum.	560	240	Cu 500	0.5	45	404	13.4
ZVI	-	1680	Cu 500	0.1	47.7	195	32

ZVI	-	240	Cu 500	0.5	47.7	28	0.9
Mix.ZVI/Pum.	560	240	Ni 50	0.5	45	404	13.4
Mix.ZVI/Pum.	560	240	Zn 50	0.5	45	404	13.4
ZVI	-	240	Ni 50	0.5	47.7	28	0.9
ZVI	-	240	Zn 50	0.5	47.7	28	0.9
Mix.ZVI/Pum.	560	240	Cu/500–Ni/50–Zn/50	0.5	45	404	13.4
Mix.ZVI/Pum.	560	240	Cu/50–Ni/50–Zn/50	0.5	45	404	13.4
ZVI	-	240	Cu/500–Ni/50–Zn/50	0.5	45	404	13.4
ZVI	-	240	Cu/50–Ni/50–Zn/50	0.5	45	404	13.4

In this study the lowest flow rate used, and assumed as representative of hypothetical field conditions, is equivalent to 0.073 $m^3m^{-2}d^{-1}$ (a column flow rate of 0.1 mL/min), which is comparable to the groundwater velocity measured inside PRBs in situ (Henderson and Demond, 2007; Li et al., 2005). The other flow rates used are 0.38 $m^3m^{-2}d^{-1}$ (equivalent to a column flow rate of 0.5 mL/min) and 1.9 $m^3m^{-2}d^{-1}$ (a flow rate of 2.5 mL/min) are examples of accelerated column test conditions.

In order to obtain information about hydrodynamic conditions in the column tests the Peclet number was calculated (Table 5-2). In fact Peclet number quantifies the relative importance of advection, molecular diffusion, and dispersion for solute transport and is therefore important for evaluating the hydrodynamic conditions of the test (Fetter, 1999; Charbeneau, 2000; Chun Kit, 2004):

$$Pe = \frac{v \cdot d}{D} \qquad \text{eq. 24}$$

The parameter v is the groundwater velocity in the longitudinal direction (m/sec), d is the mean or effective grain diameter (m), and D is the diffusion coefficient of the contaminant in an aqueous environment (m^2sec^{-1}), for which a literature value of 1.59×10^{-9} m^2/sec was used in the calculation (O et al., 2009 and references therein).

A Peclet number smaller than 0.4 indicates that solute transport is diffusion controlled, a number between 0.4 and 6 suggests a transition between diffusion control and dispersion/convection mechanisms and Pe greater than 6 indicates dominance of dispersion and convection over molecular diffusion (Fetter, 1999). Analysis of the Peclet number reveals that diffusion played a major role in tests carried out at flow rates representative of field conditions, but that dispersion and convection were not negligible. For tests employing a moderately accelerated flow rate the Peclet number was significantly higher and the role of diffusion was greatly reduced relative to field conditions. For tests at the highest hydraulic load, the Peclet number was considerably greater than 6 and the effect of diffusion was negligible. This indicates that the hydrodynamic conditions in accelerated column tests differ significantly from field conditions.

Table 5-2 Determination of Peclet number

Reactive medium	Q (ml/min)	Pe (-)
Mix. ZVI/Pum.	0.1	0.40
Mix. ZVI/Pum.	0.5	2.14
Mix. ZVI/Pum.	2.5	11.14
ZVI	0.1	0.42
ZVI	0.5	2.29
ZVI	2.5	11.92

6. BATCH TESTS: RESULTS AND DISCUSSION

6.1 Batch test program

The batch tests were carried out using as reactive media respectively ZVI and a mixture of the ZVI and pumice in different weight ratios (i.e. 10:90, 30:70, 50:50). These reactive media have been put in contact with single metal solutions of distilled water and copper nitrate (Copper(II) nitrate hydrate, purity 99.999%; Sigma-Aldrich) and nickel nitrate (Nickel(II) nitrate hexahydrate, purity 99.999%; Sigma-Aldrich) at initial concentration equal to 50 mg/l and 500 mg/l for copper and 5 mg/l and 50 mg/l for nickel. A combination of the two metals using the same concentrations was used for bi-contaminants solutions (Table 6-1) (Moraci et al., 2010a).

Table 6-1 Batch test program

Mono-contaminant batch test		**Bi-contaminant batch test**	
Reactive medium	**Contaminant**	**Reactive medium**	**Contaminants**
ZVI	Ni 5 mg/l	ZVI	Ni 5mg/l – Cu 50mg/l
ZVI/Pum. W. R.10:90	Ni 5 mg/l	ZVI/Pum. W. R.10:90	Ni 5mg/l – Cu 50mg/l
ZVI/Pum. W. R.30:70	Ni 5 mg/l	ZVI/Pum. W. R.30:70	Ni 5mg/l – Cu 50mg/l
ZVI/Pum. W. R.50:50	Ni 5 mg/l	ZVI/Pum. W. R.50:50	Ni 5mg/l – Cu 50mg/l
ZVI	Ni 50 mg/l	ZVI	Ni 5mg/l – Cu 500mg/l
ZVI/Pum. W. R.10:90	Ni 50 mg/l	ZVI/Pum. W. R.10:90	Ni 5mg/l – Cu 500mg/l
ZVI/Pum. W. R.30:70	Ni 50 mg/l	ZVI/Pum. W. R.30:70	Ni 5mg/l – Cu 500mg/l
ZVI/Pum. W. R.50:50	Ni 50 mg/l	ZVI/Pum. W. R.50:50	Ni 5mg/l – Cu 500mg/l
ZVI	Cu 50 mg/l	ZVI	Ni 50mg/l – Cu 50mg/l
ZVI/Pum. W. R.10:90	Cu 50 mg/l	ZVI/Pum. W. R.10:90	Ni 50mg/l – Cu 50mg/l
ZVI/Pum. W. R.30:70	Cu 50 mg/l	ZVI/Pum. W. R.30:70	Ni 50mg/l – Cu 50mg/l
ZVI/Pum. W. R.50:50	Cu 50 mg/l	ZVI/Pum. W. R.50:50	Ni 50mg/l – Cu 50mg/l
ZVI	Cu 500 mg/l	ZVI	Ni 50mg/l – Cu 500mg/l
ZVI/Pum. W. R.10:90	Cu 500 mg/l	ZVI/Pum. W. R.10:90	Ni 50mg/l – Cu 500mg/l
ZVI/Pum. W. R.30:70	Cu 500 mg/l	ZVI/Pum. W. R.30:70	Ni 50mg/l – Cu 500mg/l
ZVI/Pum. W. R.50:50	Cu 500 mg/l	ZVI/Pum. W. R.50:50	Ni 50mg/l – Cu 500mg/l

Batch test were carried out using 60 ml bottles containing 54 ml of contaminant solution placed in contact with 5.4 gr of reactive medium, sealed with caps, in order to set a solid-liquid ratio equal to 1:10. The vials with identical contents were tumbled and contaminant concentration was measured at designated sampling time. The sampling has been carried out at preset time intervals, sacrificing the vials, pH and Eh were measured on the specimens. Before sampling, the liquid and the solid phase were separated using a centrifuge. Supernatant liquid was sampled using pipette of 5ml and then directly injected into test tubes.

Quantitative analysis were then performed by atomic absorption spectrophotometry. All calibration curve were based on three or four standards prepared over the range of expected concentrations.

6.2 Nickel and Copper removal

Figure 6-1 shows, in semi-logaritm plot, Ni concentration over time for the four reactive media tested using mono-contaminated solutions of Ni at initial concentration of 5 and 50mg/l. As can be observed nickel removal is faster at low concentration and increasing with ZVI mass.

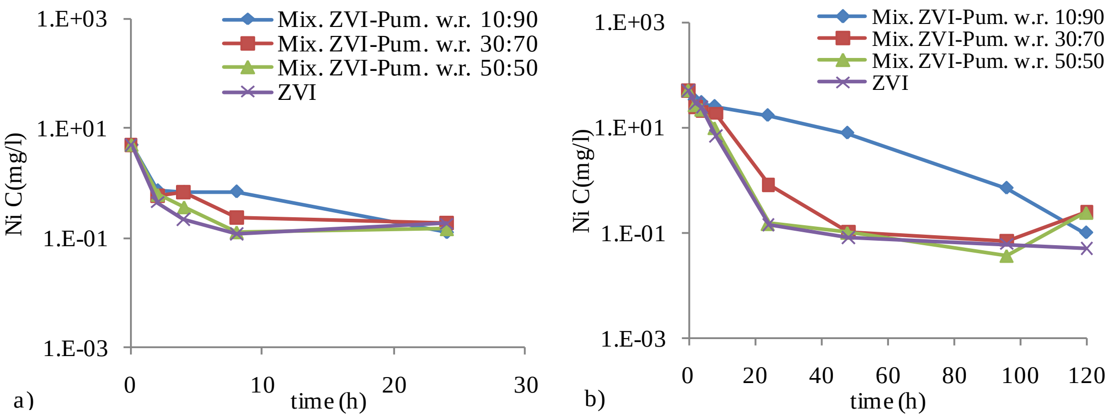


Figure 6-1 Changes of Ni concentration over time a) C_0=5mg/l and b) C_0=50mg/l

Figure 6-2 shows, in semi-logaritm plot, Cu concentration over time for the four reactive media using single metal solutions of Cu at initial concentration of 50 and 500mg/l. In this case Cu removal is faster than Ni removal and lower concentration are reached, also in this case copper removal is faster at low concentration and increasing with ZVI mass.

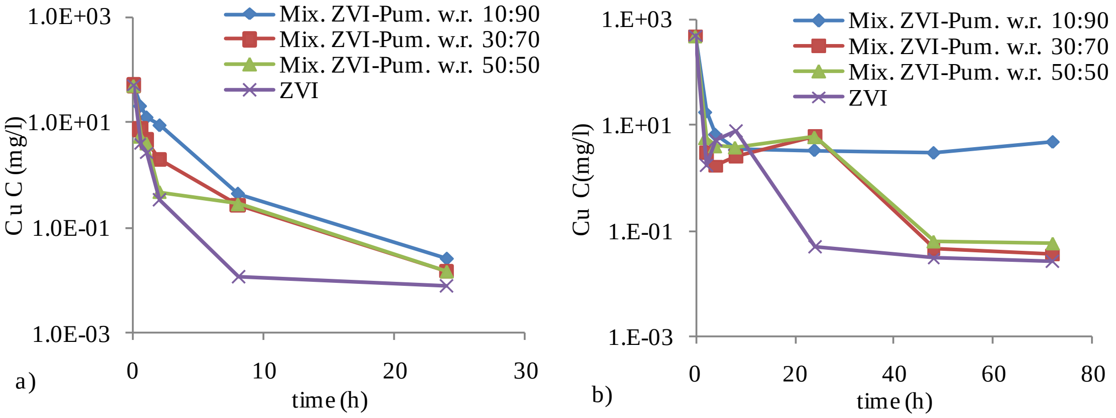
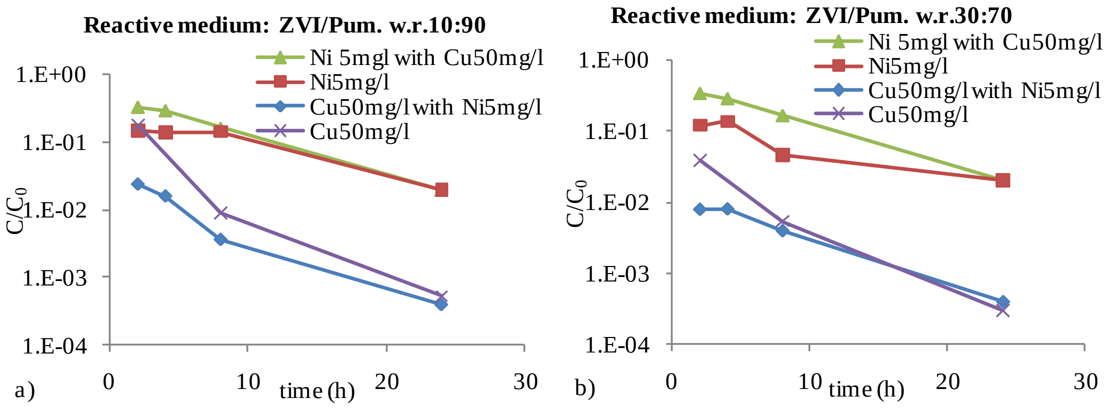


Figure 6-2 Changes of Cu concentration over time a) C_0=50mg/l and b) C_0=500mg/l

6.3 Simultaneous removal of nickel and copper

Results obtained by batch test using bi-contaminated solutions are shown in Figure 6-3, Figure 6-4, Figure 6-5, Figure 6-6 and in Table 6-2. The percentage of contaminant removed and the contaminant specific removal (ratio between the mass of contaminant removed [gr] and the mass of reactive medium [gr]) were calculated for the four reactive media.

In particular, Figure 6-3 shows changes of nickel and copper concentration over time for the four reactive media using a bi-contaminated solution of nickel and copper at initial concentration of 5 and 50 mg/l respectively and the mono-contaminated solution of Ni and Cu under the same initial concentration.



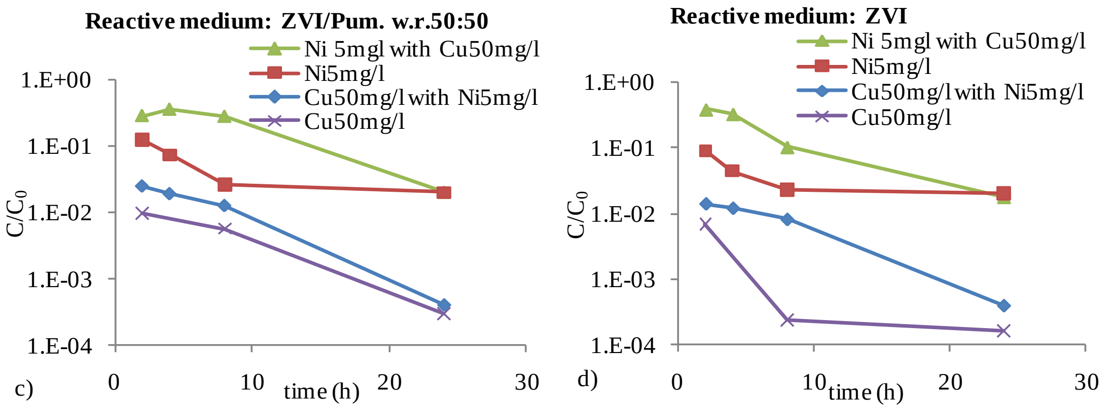


Figure 6-3 Relative concentration vs. time in mono and bi-contaminated solution of Ni5mg/l–Cu50mg/l for a) ZVI/Pum w.r.10:90 b) ZVI/Pum w.r.30:70 c) ZVI/Pum w.r.50:50 d) ZVI

At lower heavy metals concentration (i.e. Ni 5 mg/l, Cu 50 mg/l; see Figure 6-3 and Table 6-2) final concentrations of the contaminants are very close to the values obtained during mono-contaminant batch tests while removal rate is slower for nickel in presence of copper.

Figure 6-4 shows changes of metals concentration using a bi-contaminated solution of nickel and copper at initial concentration of 5 and 500 mg/l respectively and the mono-contaminated solution of Ni and Cu under the same initial concentration.

When the two metals are simultaneous present in the solution is clear the selective behaviour of the reactive media: copper is more easily removed from solution than nickel. This behaviour is more clear in Figure 6-4 where nickel concentration keeps its initial concentration value until copper is almost completely removed from solution then nickel also is removed although partially.

Figure 6-5 shows changes of metals concentration using a bi-contaminated solution of nickel and copper at initial concentration of 50 and 50 mg/l respectively and the mono-contaminated solution of Ni and Cu under the same initial concentration.

When both metals are present at the same concentration (Figure 6-5) is evident that copper removal is influenced by nickel presence.

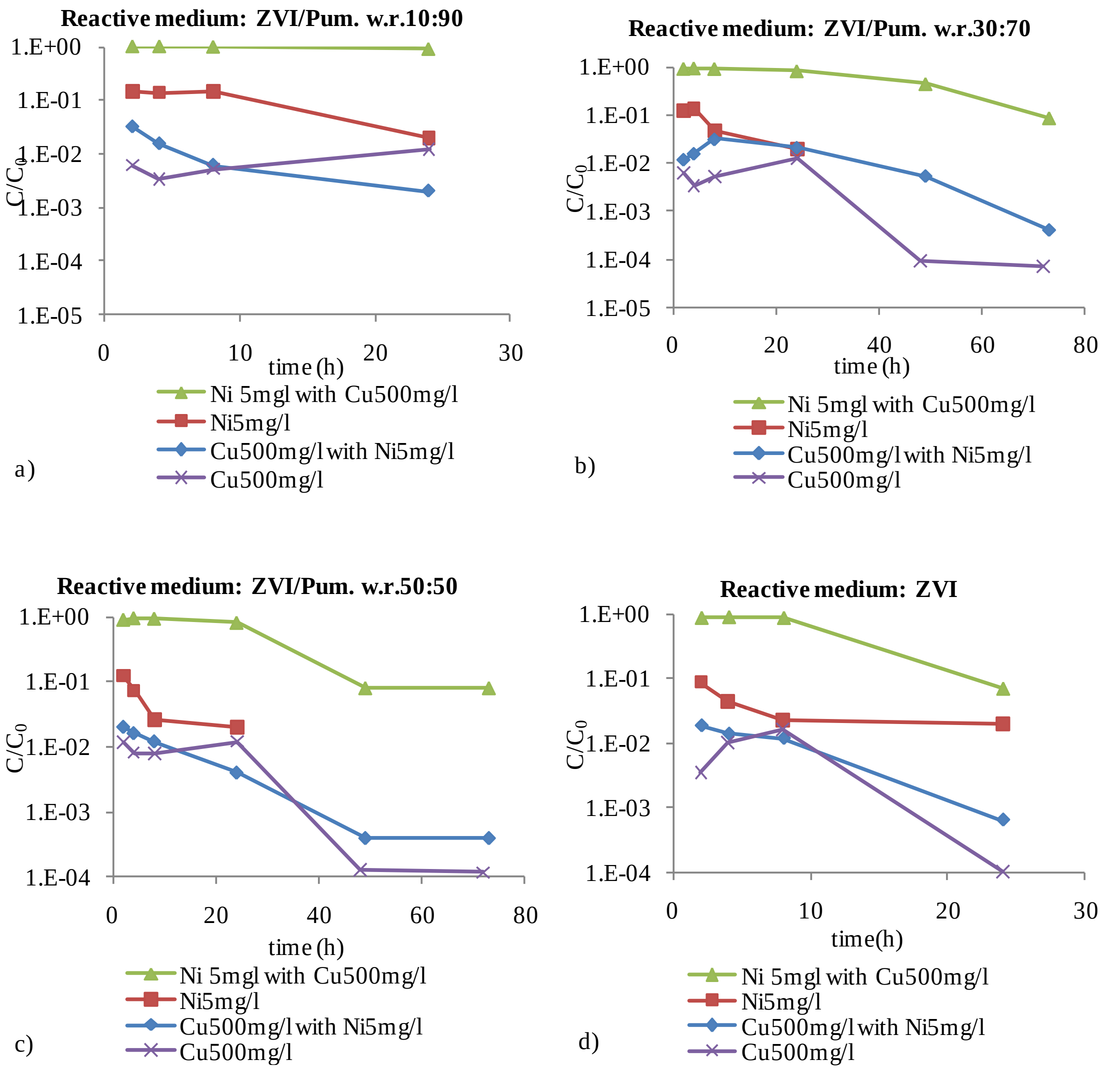


Figure 6-4 Relative concentration vs. time in mono and bi-contaminated solution of Ni5mg/l–Cu500mg/l for a) ZVI/Pum w.r.10:90 b) ZVI/Pum w.r.30:70 c) ZVI/Pum w.r.50:50 d) ZVI

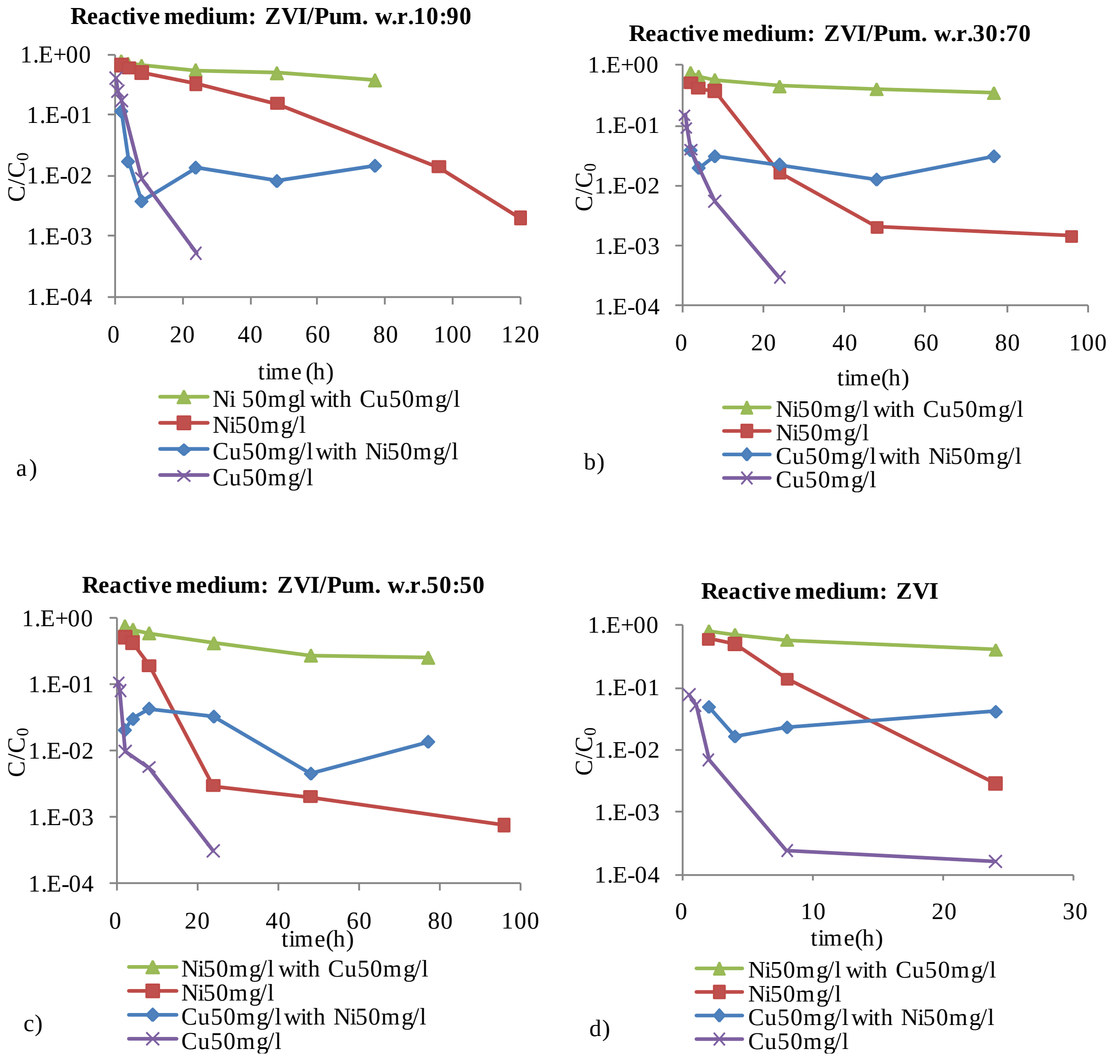


Figure 6-5 Relative concentration vs. time in mono and bi-contaminated solution of Ni50mg/l–Cu50mg/l for a) ZVI/Pum w.r.10:90 b) ZVI/Pum w.r.30:70 c) ZVI/Pum w.r.50:50 d) ZVI

Figure 6-6 shows changes of metals concentration using a bi-contaminated solution of nickel and copper at initial concentration of 50 and 500 mg/l respectively and the mono-contaminated solution of Ni and Cu under the same initial concentration.

As initial copper concentration is higher than nickel (Figure 6-6), in bi-contaminated solutions, its removal is less influenced by nickel concentration and nickel is difficulty removed.

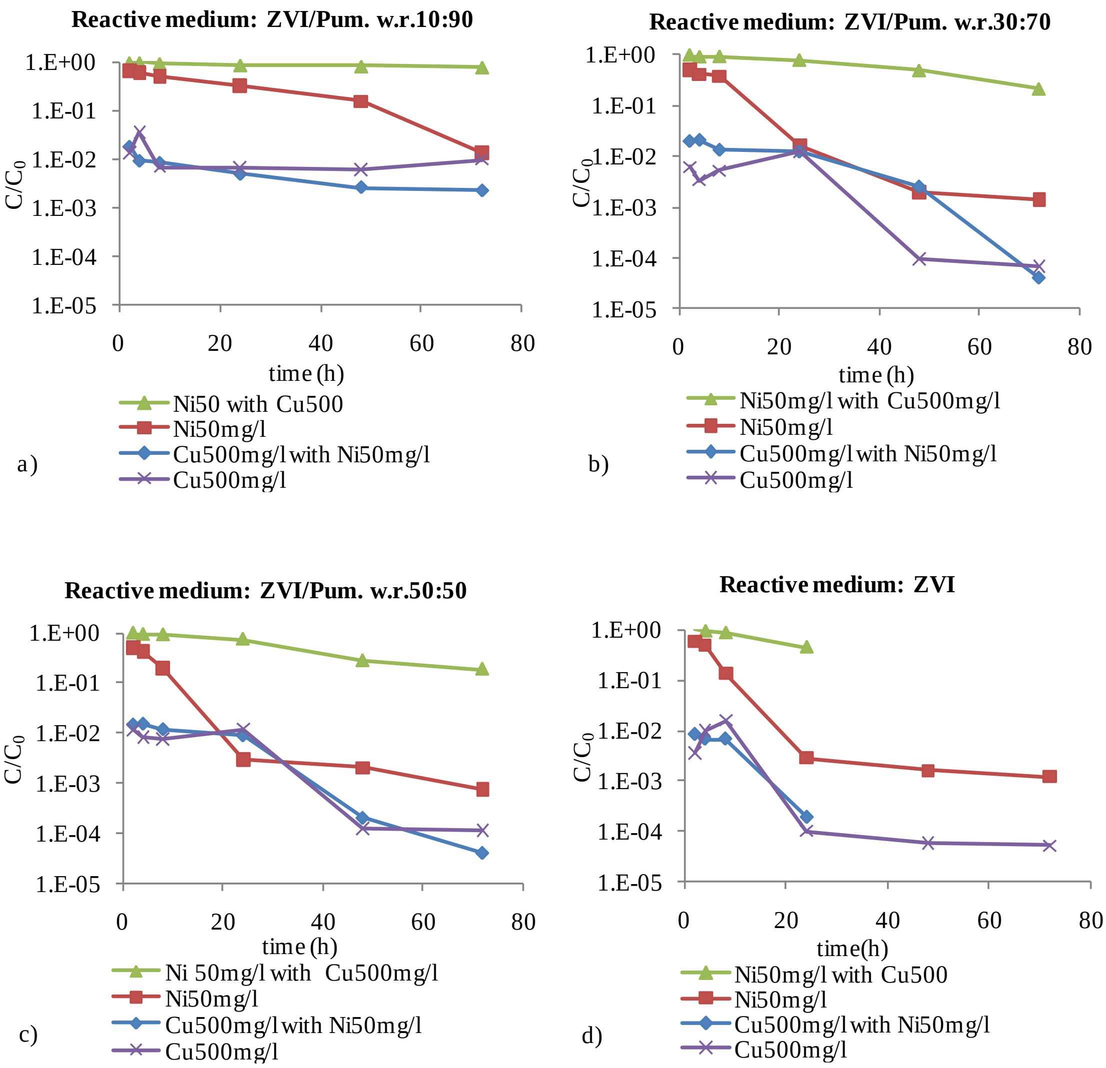


Figure 6-6 Relative concentration vs. time in mono and bi-contaminated solution of Ni50mg/l–Cu500mg/l for a) ZVI/Pum w.r.10:90 b) ZVI/Pum w.r.30:70 c) ZVI/Pum w.r.50:50 d) ZVI

Table 6-2 Batch test results

Reactive Medium	Contaminants	% Cu removal	Cu Specific Removal [g/g]	% Ni removal	Ni Specific Removal [g /g]
ZVI/Pum. w. r.10:90	Ni 5 mg/l	-	-	97,4	4,87E-05
ZVI/Pum. w. r.30:70	Ni 5 mg/l	-	-	96,22	4,81E-05
ZVI/Pum. w. r.50:50	Ni 5 mg/l	-	-	97,04	4,85E-05
ZVI	Ni 5 mg/l	-	-	96,34	4,82E-05
ZVI/Pum. w. r.10:90	Ni 50 mg/l	-	-	99,804	4,99E-04
ZVI/Pum. w. r.30:70	Ni 50 mg/l	-	-	99,5	4,98E-04
ZVI/Pum. w. r.50:50	Ni 50 mg/l	-	-	99,52	4,98E-04
ZVI	Ni 50 mg/l	-	-	99,88	4,99E-04
ZVI/Pum. w. r.10:90	Cu 50 mg/l	99,95	5,00E-04	-	-
ZVI/Pum. w. r.30:70	Cu 50 mg/l	99,97	5,00E-04	-	-

ZVI/Pum. w. r.50:50	Cu 50 mg/l	99,97	5,00E-04	-	-
ZVI	Cu 50 mg/l	99,98	5,00E-04	-	-
ZVI/Pum. w. r.10:90	Cu 500 mg/l	99,02	4,95E-03	-	-
ZVI/Pum. w. r.30:70	Cu 500 mg/l	99,99	5,00E-03	-	-
ZVI/Pum. w. r.50:50	Cu 500 mg/l	99,99	5,00E-03	-	-
ZVI	Cu 500 mg/l	99,99	5,00E-03	-	-
ZVI/Pum. w. r.10:90	Ni 5mg/l–Cu 50mg/l	99,99	5,00E-04	99,99	5,00E-05
ZVI/Pum. w. r.30:70	Ni 5mg/l–Cu 50mg/l	99,99	5,00E-04	99,99	5,00E-05
ZVI/Pum. w. r.50:50	Ni 5mg/l–Cu 50mg/l	99,99	5,00E-04	99,99	5,00E-05
ZVI	Ni 5mg/l–Cu 50mg/l	99,99	5,00E-04	99,99	5,00E-05
ZVI/Pum. w. r.10:90	Ni 5mg/l–Cu 500mg/l	99,84	4,99E-03	18,52	9,26E-06
ZVI/Pum. w. r.30:70	Ni 5mg/l–Cu 500mg/l	99,99	5,00E-03	91,12	4,56E-05
ZVI/Pum. w. r.50:50	Ni 5mg/l–Cu 500mg/l	99,99	5,00E-03	92	4,60E-05
ZVI	Ni 5mg/l–Cu 500mg/l	99,93	5,00E-03	92,74	4,64E-05
ZVI/Pum. w. r.10:90	Ni 50mg/l–Cu 50mg/l	98,54	4,93E-04	62,1	3,11E-04
ZVI/Pum. w. r.30:70	Ni 50mg/l–Cu 50mg/l	96,98	4,85E-04	64,64	3,23E-04
ZVI/Pum. w. r.50:50	Ni 50mg/l–Cu 50mg/l	98,62	4,93E-04	74	3,70E-04
ZVI	Ni 50mg/l–Cu 50mg/l	95,93	4,80E-04	60,08	3,00E-04
ZVI/Pum. w. r.10:90	Ni 50mg/l–Cu 500mg/l	99,77	4,99E-03	20	1,00E-04
ZVI/Pum. w. r.30:70	Ni 50mg/l–Cu 500mg/l	99,99	5,00E-03	78,94	3,95E-04
ZVI/Pum. w. r.50:50	Ni 50mg/l–Cu 500mg/l	99,99	5,00E-03	81,2	4,06E-04
ZVI	Ni 50mg/l–Cu 500mg/l	99,33	5,00E-03	54,5	2,73E-04

Nickel removal can be interpreted with the usual first-order kinetic (eq.1).

The values of the kinetic constant are listed in Table 6-3. In bi-contaminated solution k values are strongly reduced.

As can be observed in Figure 6-7 where k values are represented as function of ZVI percentage present in the mixture, for mono-contaminant batch tests, it seems that starting from the 50:50 ZVI/Pumice mixtures the effect of an increase of ZVI in the mixture is rather negligible. The kinetic of nickel removal for bicontaminant batch tests carried out using a contaminated solution containing 50 mg/l copper and 500 mg/l nickel is about one order of magnitude slower.

Table 6-3 Nickel kinetic constants

	Reactive media			
Contaminated Solution	10:90	30:70	50:50	ZVI
Ni50mg/l	0.048	0.138	0.239	0.242
Ni50mg/l-Cu500mg/l	0.003	0.019	0.023	0.03

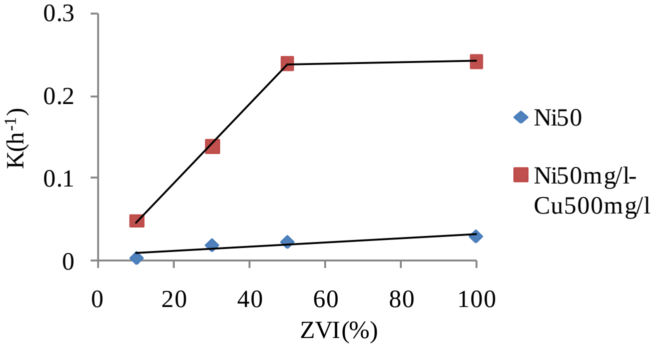
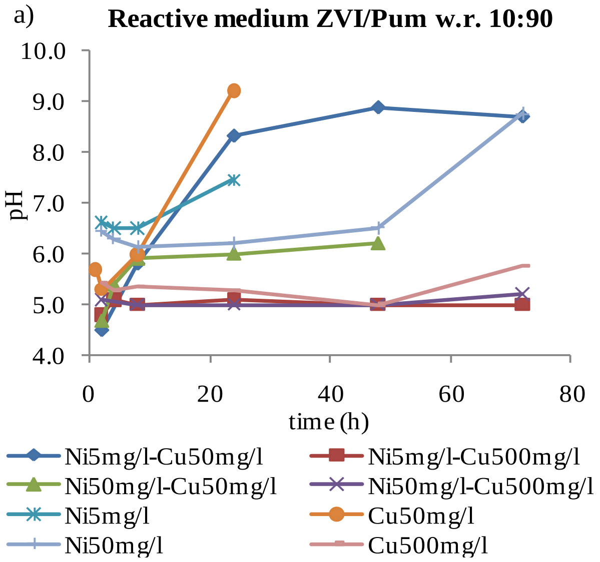


Figure 6-7 kinetic rate constant vs. ZVI (%)

It is not possible to interpret with the first-order kinetic the removal of nickel (only when the lowest concentration is used) and that of copper because of the low concentration values already reached at the first sampling.

6.4 Ph measurements

During batch tests it has been observed a fast pH increase (Figure 6-8) after the complete removal of contaminants from solution while during the progress of the reaction the pH increase is moderate.



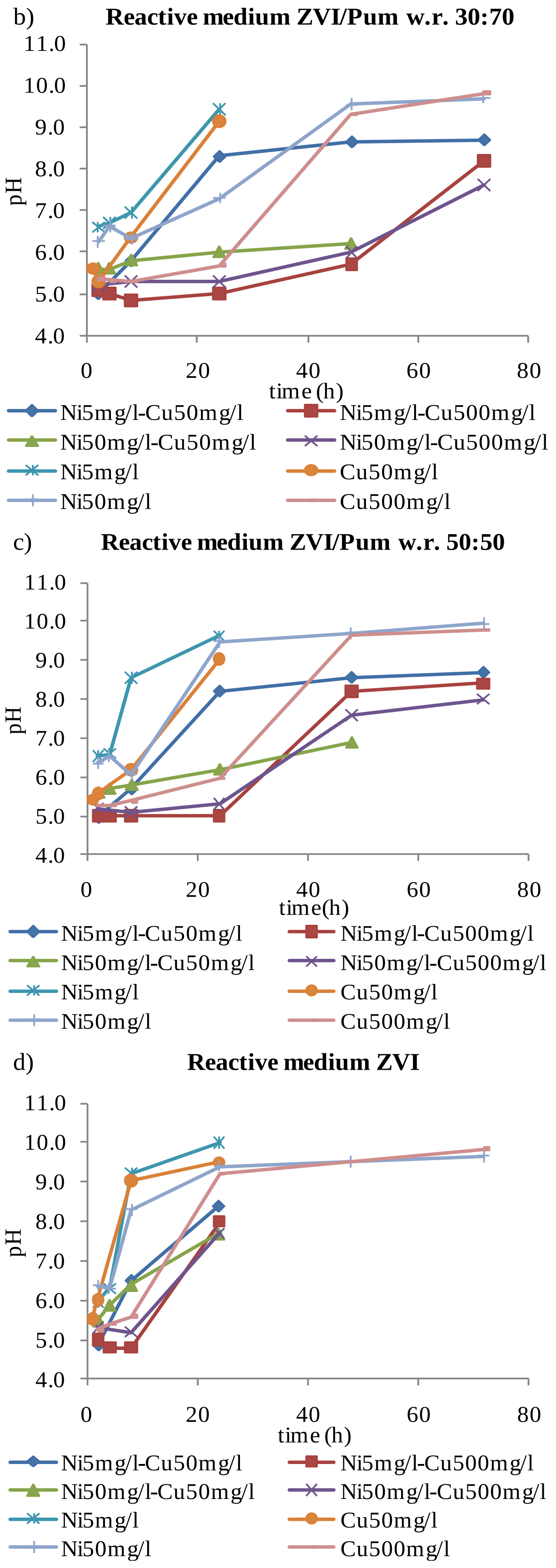


Figure 6-8 pH vs. time in mono and bi-contaminated solution for a) ZVI/Pum. w.r. 10:90 b) ZVI/Pum. w.r. 30:70 c)ZVI/Pum. w.r.50:50 and d)ZVI.

6.5 Considerations about metals removal mechanisms

Through pH measurements carried out during the test, it was possible to draw some considerations about possible metals removal mechanisms and iron corrosion.

At early stage, when the medium reveals its maximum reactivity, pH remains rather constant close to its initial value and an increment can be observed when Copper and Nickel are progressively removed, this fact can be also observed for mono-contaminated solutions. An explanation of this phenomenon could be that, initially, ZVI is probably oxidized from the oxidized form of the contaminant (Ox) which reduction yields a corresponding reduced form (Red) of the same contaminant according the following equation:

$$Fe^0+Ox \rightarrow Fe^{2+}+Red \qquad \text{eq. 24}$$

This is a spontaneous electrochemical process, known as cementation that involves the reduction of a more electropositive (noble) species by more electronegative (sacrificial) metals (e.g. Fe^0). The ‘‘cementation’’ process, implying that redox-sensitive compounds are reduced into insoluble forms, has been shown to be highly effective under acidic conditions in the absence of dissolved oxygen (Rangsivek et al., 2005).

The cementation process for copper can be described by the following redox reaction (Diels et al., 2002; Bartzas et al., 2006; Komintasas et al., 2007):

$$Fe^0+Cu^{2+}\rightarrow Fe^{2+}+Cu_0 \qquad \text{eq.25}$$

This reaction is possible as copper standard redox potential is higher than the one of ZVI ($E_{Fe2+/Fe}$= -0,44 V and $E_{Cu2+/Cu}$=0,34 V).

Nickel participates also in a cementation reaction in ZVI systems and the product of the cementation reaction is the noble species in a metallic form (Ni_0) (Dries et al., 2005). This reaction is possible as nickel standard redox potential is slightly higher than Fe^{2+}/Fe^0 ($E_{Ni2+/Ni}$ = - 0.264 V) but it is less favored than in the case of copper . In the case of simultaneous presence of Nickel and Copper in aqueous solution, Copper, whose standard redox potential is significantly higher than the one of Nickel, represents the main oxidant agent. For this reasons Copper removal is probably favoured respect to Nickel removal. The fast increase of pH, after contaminants removal, is probability due to ZVI oxidation by water that, in anaerobic conditions, can be expressed by the following equation:

$$Fe^0+2H_2O\rightarrow Fe^{2+}+H_2 +2OH \qquad \text{eq.26}$$

The process of H_2O reduction by Fe^0 obviously reduces the efficiency of the decontamination process, H_2O acts as concurrent for contaminant (Noubacteb, 2009); the slower removal of Nickel especially at high concentration could be due to this competition. During batch tests a reduction process, as mechanism of contaminants removal, is promoted respect to adsorption and coprecipitation process, especially at early stages also because of effective mixing.

6.6 Conclusions

A series of batch tests was carried out on granular mixture of ZVI/Pumice at different weigh ratio (10:90, 30:70, 50:50, 100:0) using mono-contaminated solutions and bicontaminated solutions of Nickel, at concentration of 5mg/l and 50mg/l, and Copper at concentration of 50mg/l and 500mg/l, ZVI was also used as benchmark. According to the tests results the following considerations can be drawn:

- ZVI/Pumice mixtures in different weigh ratio are reactive toward Ni and Cu;
- ZVI and the granular mixtures of ZVI/Pumice at different weight ratio reveal a selective behaviour toward the two heavy metals: Copper is, in fact, more easily removed from solution and reactions involving Nickel usually begin after complete Copper removal.
- the fast increase of pH, after complete contaminants removal, suggests that, at early stages of batch test, the cementation process, as metal removal mechanism, is the main.

7. COLUMN TESTS: SINGLE-METAL SOLUTIONS

7.1 Introduction

Column tests are normally used in order to obtain permeable reactive barriers design parameters (e.g. mass of reactive medium, barrier thickness, reaction kinetic parameters). As described in chapter 4 a column test can be carried out under different flow rate and contaminant concentration conditions that can more or less reflect the real field conditions. Generally, lower values of flow rate approximate better the in situ conditions but these circumstances imply a longer period of time until the exhaustion (breakthrough) of the reactive medium can be reached. While accelerated-flow column tests are a more resource-intensive methods for evaluating the longevity of a reactive medium (Gavaskar et al., 2000); these tests are not directly required for designing the PRB; however, they provide a mean of accelerating the aging of the iron by passing groundwater at a significantly faster rate through the column with reactive medium than would occur at the field site. The advantage of accelerated flow test is that many pore volumes of contaminated groundwater can be flowed through the reactive medium in a short time to simulate several years of operation of the field PRB (Gavaskar et al., 2000). Accelerated-flow tests may be considered more an area of investigation for PRB technology developers than for site owners considering routine PRB application (Gavaskar et al., 2000).

The column tests carried out in the initial phase of the experimental activity had the main objective to study the efficiency of the innovative reactive medium constituted by a ZVI and Pumice granular mixture for heavy metals contaminated groundwater. The tests were conducted under different flow rate and contaminant concentration conditions in order to study the following factors:

4. The effect of the nickel contaminant concentration;
5. The effect of flow rate;
6. Accelerated column tests: by means of higher flow rate or higher contaminant concentration respect to in situ conditions.

7.2 Column tests setting

The reactive medium used in the column tests is a granular mixture of ZVI and pumice with a weight ratio of 30:70 because in previous studies (Moraci et al., 2010b; Suraci, 2011; Calabrò et al., 2011) this specific weight ratio has shown to be a good compromise between the reactivity (higher ZVI content) and long term hydraulic performance (higher pumice content). Systems with ZVI alone were also investigated and used as benchmarks.

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

In Table 7-1 and in Table 7-2 are summarized the main information of column tests where solutions contaminated respectively by nickel and copper were used. The concentrations used were 8, 40 and 95 mg/l for nickel and 500 mg/l for copper.

The tests using Nickel solutions were carried out at three flow rates (0.1, 0.5, 2.5 ml/min). While the tests using copper solutions were performed at two flow rates (0.5 – 0.1 ml/min). All the tests using the ZVI/Pumice granular mixture were performed using 240 g of ZVI and 560 g of pumice. The benchmark tests on ZVI were carried out at flow rate of 0.1 and 2.5 ml/min using 1680 g of ZVI, while the benchmark tests carried out at flow rate of 0.5 ml/min using 240 g of ZVI.

The tests were continued until a major loss in reactivity or a reduction in the hydraulic conductivity of at least three orders of magnitude were observed.

Table 7-1 Column tests carried out with nickel solutions

Reactive Medium	Pumice [g]	ZVI [g]	Cont.Conc. [mg/L]	Flow rate (mL/min)	Test duration [d]
Mix. ZVI/Pum.	560	240	8	2.5	110
Mix. ZVI/Pum.	560	240	40	2.5	32
Mix. ZVI/Pum.	560	240	95	2.5	27
Mix. ZVI/Pum.	560	240	40	0.5	160
Mix. ZVI/Pum.	560	240	40	0.1	588
ZVI	-	1680	8	2.5	14*
ZVI	-	1680	40	2.5	30
ZVI	-	1680	95	2.5	52
ZVI	-	240	40	0.5	52
ZVI	-	1680	40	0.1	404

* test forcedly stopped because of column clogging

Table 7-2 Column tests carried out with copper solutions

Reactive Medium	Pumice [g]	ZVI [g]	Cont.Conc. [mg/L]	Flow rate (mL/min)	Test duration [d]
Mix. ZVI/Pum.	560	240	500	0.1	683
Mix. ZVI/Pum.	560	240	500	0.5	70
ZVI	-	1680	500	0.1	598*
ZVI	-	240	500	0.5	58*

* test forcedly stopped because of column clogging

Figure 7-1 and Figure 7-2 show the apparatus used for column tests and described in §4.7. Only for the tests carried out with ZVI and a flow rate of 0.1 ml/min column of 100 cm of length were used (Figure 7-1).

Figure 7-1 100 cm column

Figure 7-2 50 cm column

7.3 Effect of nickel concentration

Figure 7-3, Figure 7-4 and Figure 7-5 show breakthrough curve at three different sampling ports (3, 18, 28 cm) versus time for the mixture ZVI/Pumice column system using solutions contaminated by Nickel at initial concentration of 8, 40 and 95 mg/l respectively. The flow rate used was of 2.5 ml/min in order to reach reactive medium exhaustion in a short period. C/C_0 is the normalized concentration, C is the effluent concentration and C_0 is the average influent concentration over the entire experimental duration.

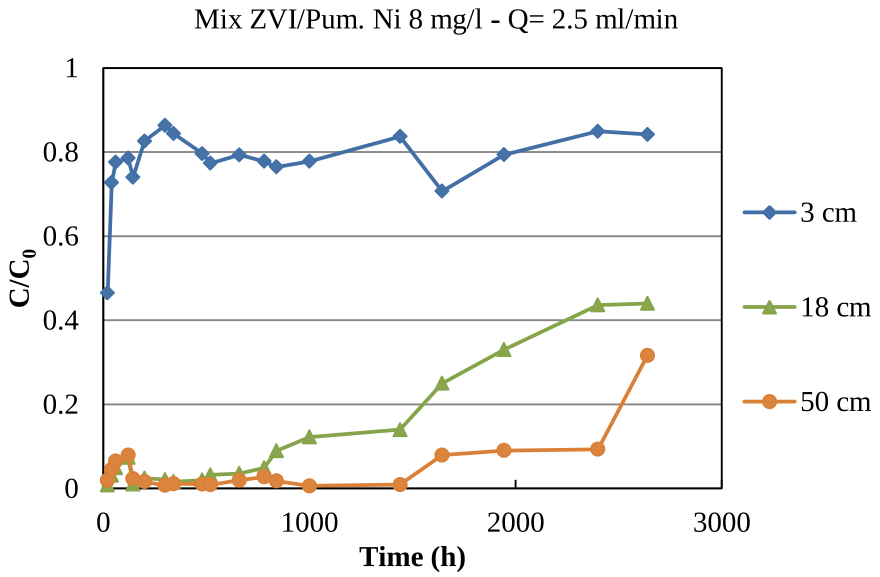


Figure 7-3Ni breakthrough curve at different sampling ports versus time in the mixture ZVI/Pumice (C_0=8mg/l)

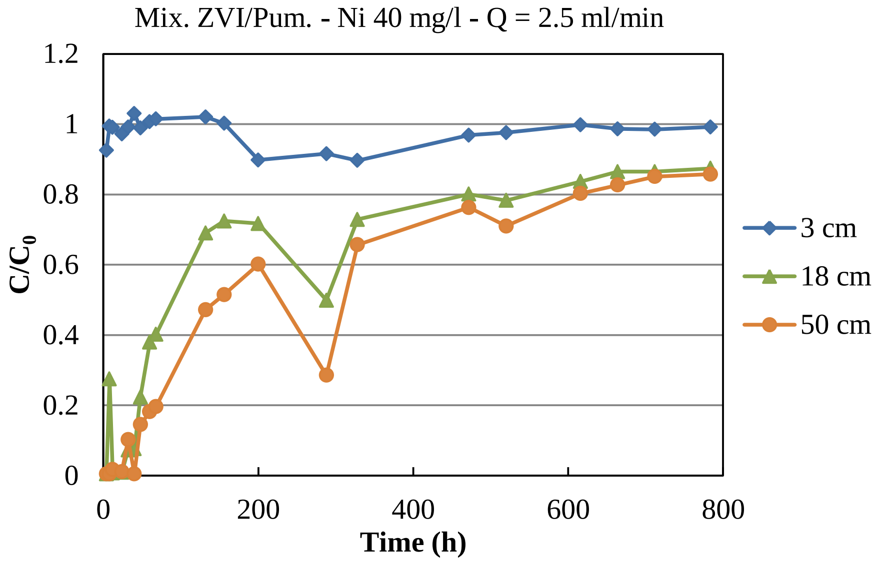


Figure 7-4 Ni breakthrough curve at different sampling ports versus time in the mixture ZVI/Pumice (C_0=40mg/l)

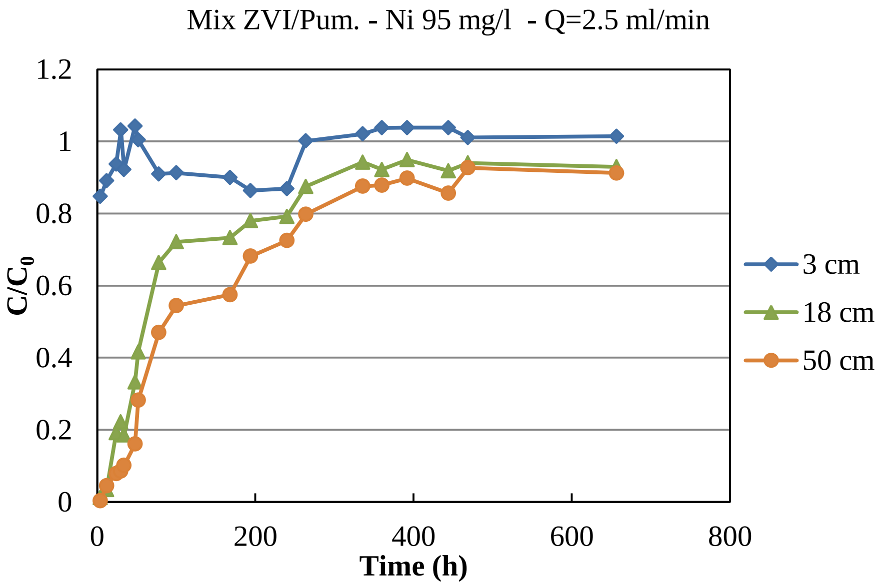


Figure 7-5 Ni breakthrough curve at different sampling ports versus time in the mixture ZVI/Pumice (C_0=95mg/l)

Ni concentration at sampling port located at 50 cm is maintained below a concentration of 1 mg/l (C/C_0 = 0.125) over a long period (2400 h or 888 PV) when it is present in the solution with an initial concentration of 8 mg/l.

When initial nickel concentration is 40 or 95 mg/l, Ni concentration measured at the outlet of the columns increases rapidly exceeding the concentration of 1 mg/l (C/C_0 = 0.025 or 0.01) respectively after 24 h, or 8.8 PV, and 4 h, or 1.5 PV.

Figure 7-6 Figure 7-7 and Figure 7-8 show breakthrough curve at three different sampling ports (3, 18, 28 cm) versus time in the ZVI column systems. It must be underlined that in these systems was used a mass of ZVI 7 times greater than that used in the mixture.

For the column test where the lowest nickel concentration is used, the values measured at 3 cm of column length, were only represented (Figure 7-6) because the other values measured are below detection limit of the instrument. In the latter column experiment nickel is removed for all the duration of the test (14 days) starting from the first sampling port (located at 3 cm of column length). The short duration of the test, due to the column clogging, did not allow to observe the exhaustion of the medium reactivity.

When initial nickel concentration is 40 or 95 mg/l Ni concentration measured at the outlet of the columns increases rapidly exceeding a concentration of 1 mg/l (C/C_0 = 0.025 or 0.01) respectively after 200 h, or 154 PV, and 168 h, or 129 PV.

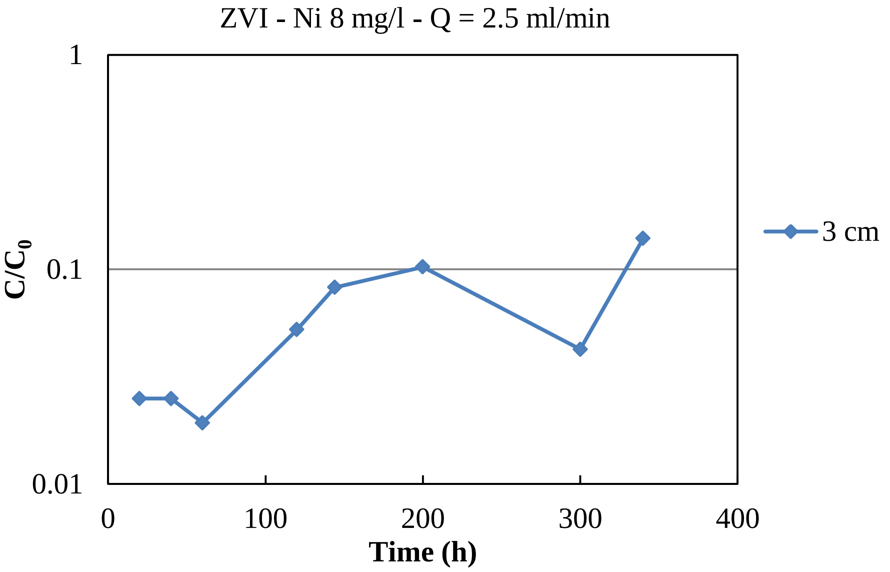


Figure 7-6 Ni breakthrough curve at different sampling ports versus time in the ZVI (C_0=8mg/l)

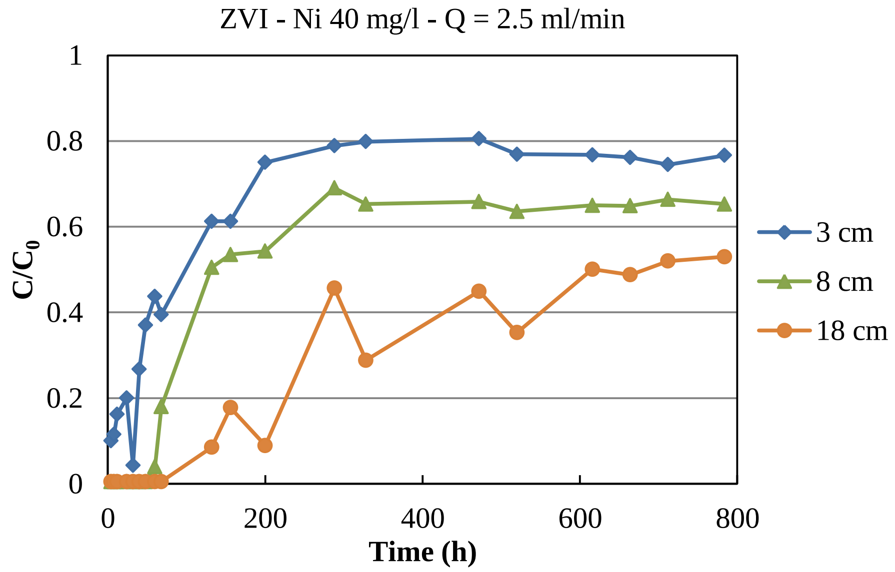


Figure 7-7 Ni breakthrough curve at different sampling ports versus time in the ZVI (C_0=40mg/l)

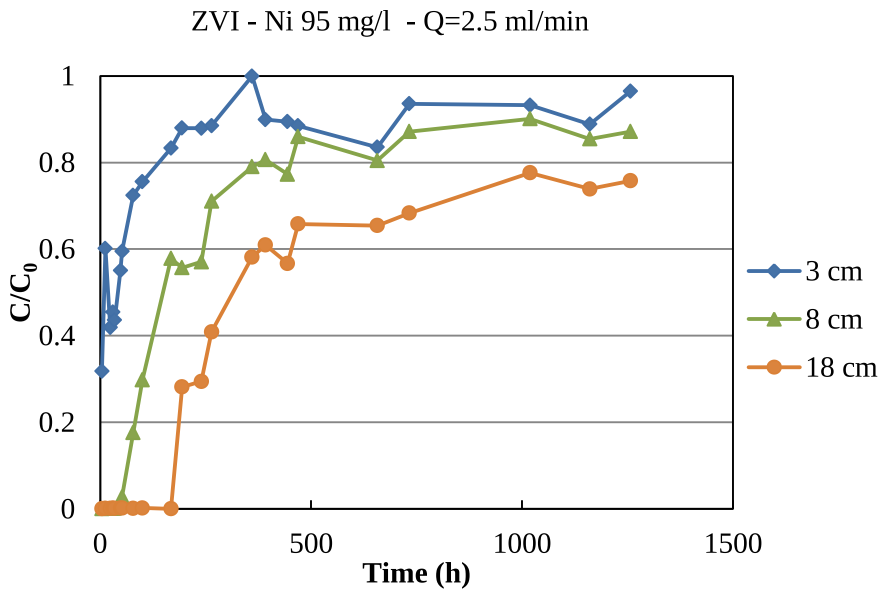


Figure 7-8 Ni breakthrough curve at different sampling ports versus time in the ZVI (C_0=95mg/l)

7.3. 1 Effect of nickel concentration on reactive medium removal capacity

In order to evaluate the effect of Ni concentration on the removal capacity of the mixture ZVI/ Pumice, Figure 7-9 shows, for the column tests carried out using initial nickel concentration equal to 8, 40 and 95 mg/l, the nickel mass discharged from the outlet of the columns as a function of the nickel mass in input. In the same figure is represented the line called “no removal” which represents the situation where the medium is not reactive and the contaminant is not removed from solution.

The highest removal efficiency is registered for the lowest initial nickel concentration. The test carried out using a flow discharge of 2.5 ml/min and an initial nickel concentration of 95 mg/l shows slightly better results that those carried out using a 40 mg/l initial concentration. This could indicate that, for extremely high nickel concentrations, (the value of 40 mg/l is 2000 times higher than the maximum value allowed in Italy and 95 mg/l is 4750 times higher), the performance of the reactive medium is influenced by the concentration only in a very limited extent due to the rapid exhaustion of the reactive sites.

In the same flow rate condition and using the same contaminant solutions, column tests using only ZVI were carried out and used as benchmarks. Column test carried out using ZVI and an initial nickel concentration of 8 mg/l had a short duration (14 days) because was forcedly interrupted due to column clogging incompatible with the high value of flow rate used, the test was reproduced two times in order to test the repeatability of the clogging.

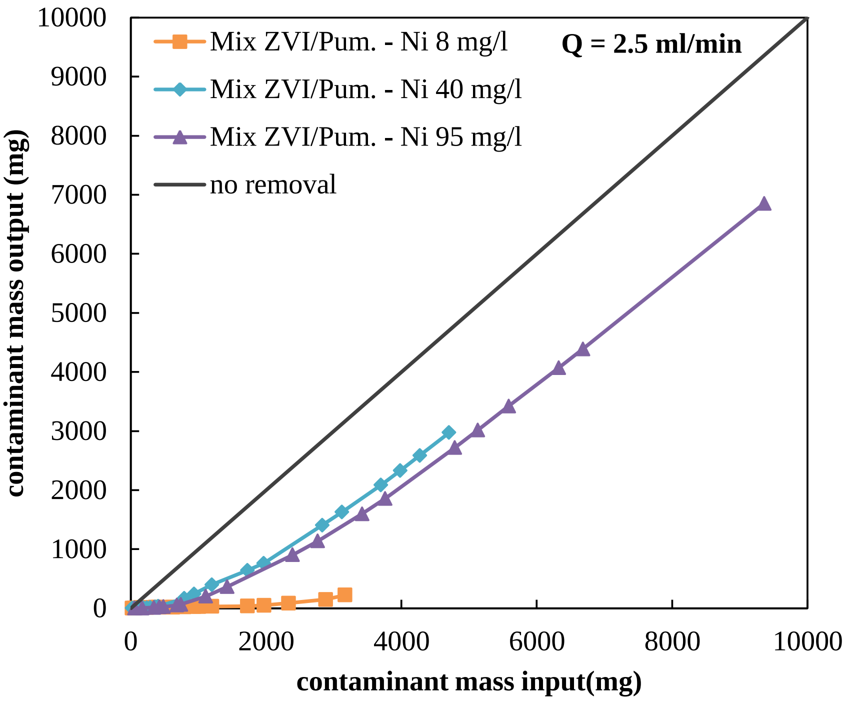


Figure 7-9 Nickel mass discharge from the outlet of columns vs. nickel mass in input for different values of initial Nickel concentration and a flow rate of 2.5 ml/min

Figure 7-10 and Figure 7-11 show the nickel mass discharged from the outlet of the columns as a function of the nickel mass in input for column tests carried out using the mixture ZVI/Pumice and ZVI alone for respectively the first 4000 mg and 800 mg of nickel flowed into the column for a better visualization of the results. The “no removal” line is also shown. The output for column tests carried out with ZVI using a mass of 1680 gr is considered at 3 cm from column inlet in order to consider the same amount of ZVI present in the mixture. As observed for the mixture ZVI/Pumice (Figure 7-9), if the reactive medium constituted by the only ZVI is considered, the best performance in term of contaminant removal is observed for the lowest contaminant concentration (Figure 7-11) instead with solutions contaminated by nickel with higher initial concentration (i.e. 40 and 95 mg/l) the removal capacity is almost similar.

A comparison between the mixture ZVI/Pumice and ZVI when the same amount of ZVI is used, which means a column length of 50 cm and 3 cm respectively, shows the better performance of the mixture. Whereas nickel needs a long residence time until it can be removed from solution, the mixture shows higher removal efficiency than ZVI in fact it can assure a longer residence time than ZVI.

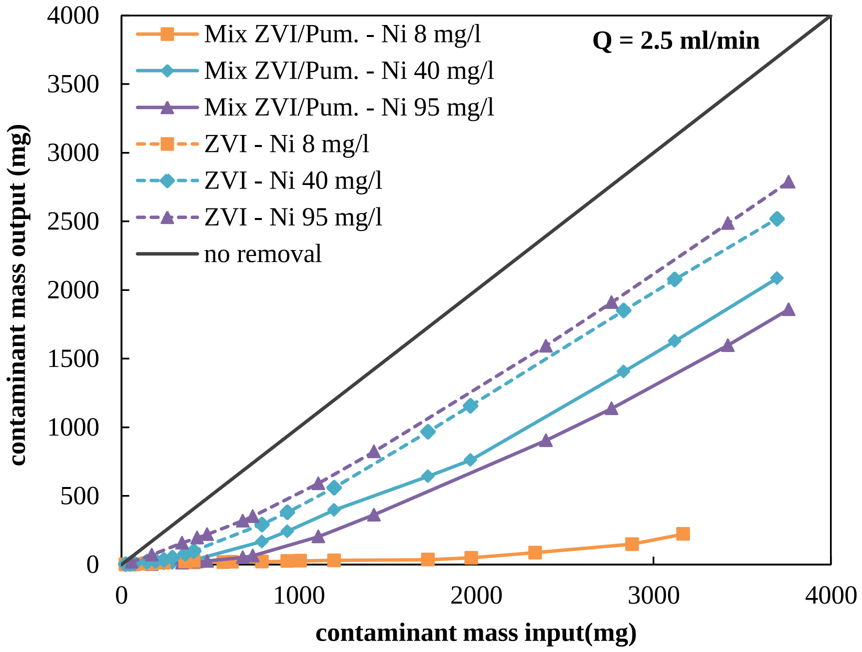


Figure 7-10 Nickel mass discharge from the outlet of columns vs. nickel mass in input for different values of initial Nickel concentration and a flow rate of 2.5 ml/min (for the first 4000 mg of nickel flowed into the column)

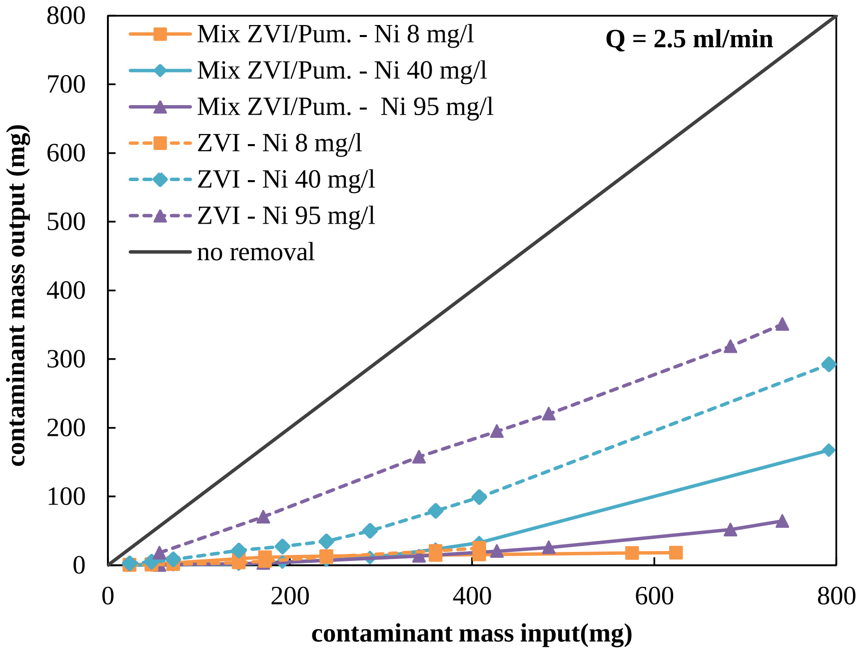


Figure 7-11 Nickel mass discharge from the outlet of columns vs. nickel mass in input for different values of initial Nickel concentration and a flow rate of 2.5 ml/min (for the first 800 mg of nickel flowed into the column).

In order to characterize the capability of tested materials for contaminant removal and in order to compare the two reactive media tested, the specific removal capacity related to ZVI only (SRC_{ZVI}) was calculated using eq. 22 (Chapter 5).

The values of SRC_{ZVI} were calculated considering the entire mass of ZVI present in the column: 240 gr for the mixture and 1680 gr for the ZVI. The specific removal capacity related to 240 gr of ZVI, $SRC_{ZVI\ (240\ gr)}$, refers to the 3 cm and 50 cm of column length for the ZVI and for the ZVI/Pumice mixture respectively (Table 7-3).

The SRC_{ZVI} values of the mixture ZVI/pumice are higher than those calculated for the ZVI, showing the positive effect of the pumice in maintaining and improving the typical removal capacity of ZVI. The pumice can contribute to contaminant removal probably thanks to the possible removal mechanisms described in chapter 4 and due to its capacity of storing corrosion products in its pores thus augmenting the available reactive surface for the reactions. The higher $SRC_{ZVI\ (240gr)}$ values of the mixture ZVI/Pumice than ZVI are probably due to the higher residence time guaranteed by the pumice when the same ZVI mass is considered.

Table 7-3 Specific removal capacity

Reactive medium	Cont.Conc. [mg/L]	Poll. Mass flowed [mg]	SRC_{ZVI} [g/g]	$SRC_{ZVI\ (240gr)}$ [g/g]
ZVI	8	408	2.38E-04	1.06E-03
ZVI/Pum.	8	408	1.72E-03	1.72E-03
ZVI	40	4704	2.28E-03	6.28E-03
ZVI/Pum.	40	4704	7.15E-03	7.15E-03
ZVI	95	6327	3.16E-03	5.24E-03
ZVI/Pum	95	6327	9.67E-03	9.67E-03

During column tests, measures of pH were also carried out on the samples withdrawn from the various sampling ports located along column. These measurements show, for all column tests, an increase of pH along column distance starting from a value of 6.5 and up to values between 9 and 11, these pH values decrease with the progress of the experiment until the initial pH value is restored. Figure 7-12 shows pH values measured at the outlet of column test as function of contaminant mass in input to the column. The higher values refer to the columns where the only ZVI was used, but it is important to underline that ZVI mass is seven time greater than ZVI mass used in the mixture. pH increase is due to ZVI oxidation by water, so it can be stated that this effect is more relevant when a great mass of ZVI is used and when a low value of contaminant concentration is used.

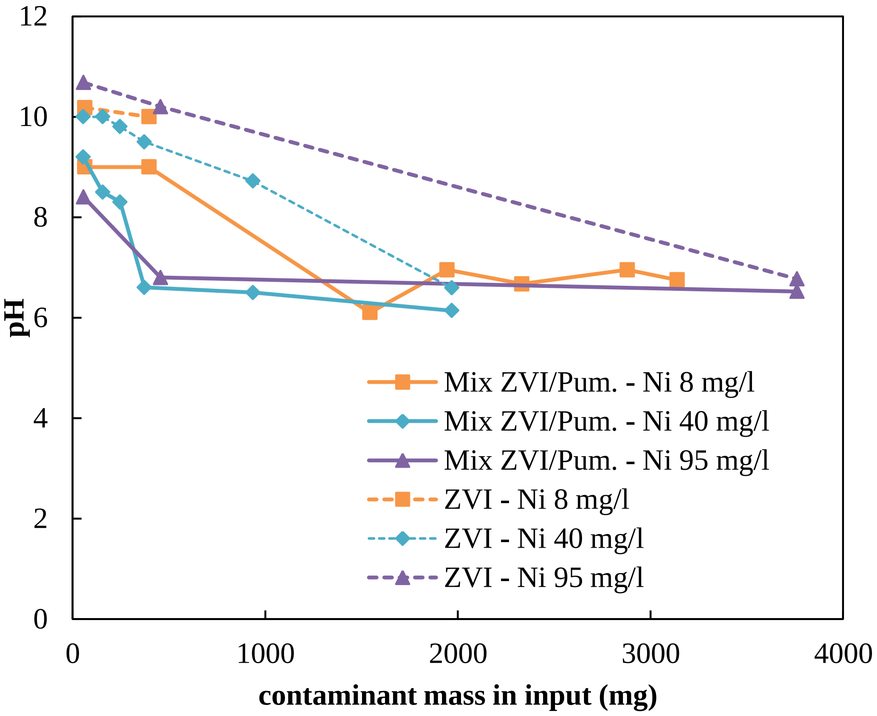


Figure 7-12 pH values vs. contaminant mass in input for column tests carried out with a flow rate equal to 2.5 ml/min

7.3. 2 Effect of nickel concentration on reactive media hydraulic conductivity

The hydraulic conductivity has been determined during the tests in order to evaluate the long term hydraulic behaviour of the reactive media tested.

Figure 7-13 and Figure 7-14 show the profile of the hydraulic conductivity plot against the contaminant mass flowed into the column and as function of time for the tests performed using a flow rate of 2.5 ml/min and nickel solutions. The hydraulic conductivity profiles emphasize the ability of the mixture ZVI/pumice to maintain an adequate permeability for a time longer than that evidenced by the ZVI alone. The hydraulic conductivity is almost constant for columns filled with a mixture ZVI/pumice, using an initial nickel concentration equal to 40 and 95 mg/L. In the columns filled with ZVI, in the same test conditions, the hydraulic conductivity decreased at the end of the test of almost three and two orders of magnitude respectively.

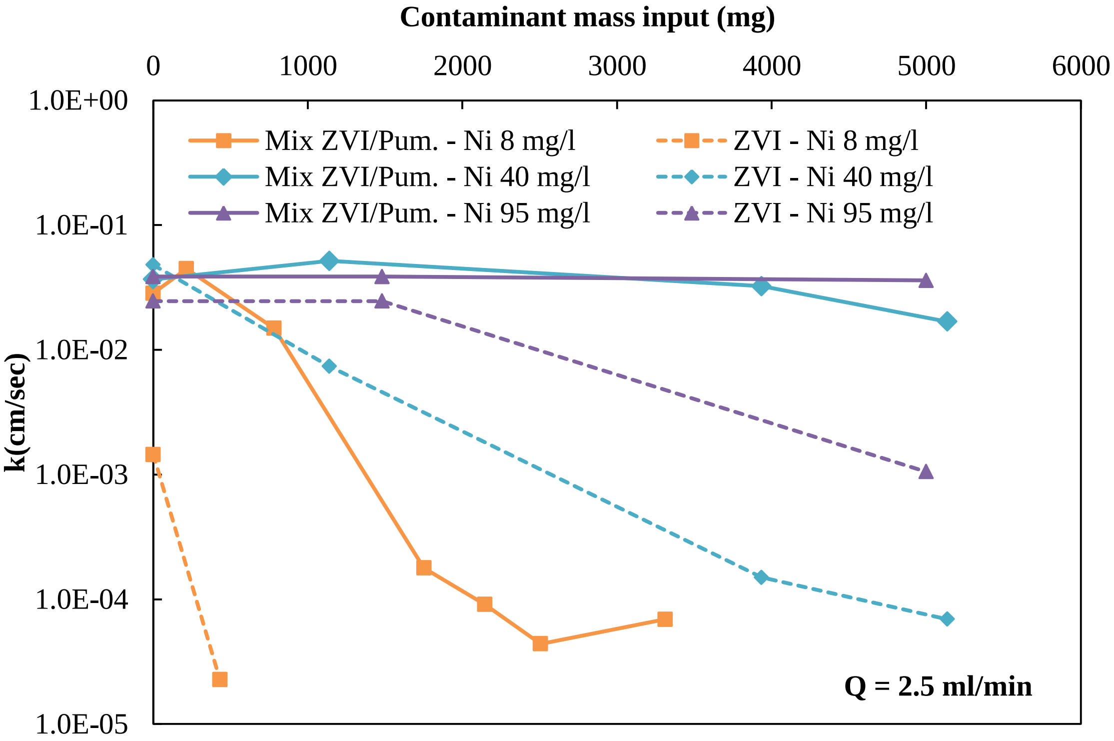


Figure 7-13 Hydraulic conductivity vs. contaminant mass input for column tests carried out at different values of initial nickel concentration

As previously mentioned, the column test, carried out using ZVI alone with initial nickel concentration equal to 8 mg/L, was interrupted forcedly after 340 h due to the permeability reduction; the measurement revealed an hydraulic conductivity of $2.2 \cdot 10^{-5}$ cm/sec incompatible with the high flow rate used. The column test was repeated two times in order to confirm the result. The mixture ZVI/pumice, in the same test conditions, revealed a hydraulic conductivity equal to $6.9 \cdot 10^{-5}$ cm/sec only after 2640 h of operation.

The rate permeability decline in the course of time increases with decreasing of nickel concentration or equivalently with increasing of removal capacity of the medium, as previously observed. It can be stated that reactive media showing greater removal efficiencies evidence a greater reduction of the hydraulic conductivity with time.

Oxidation of ZVI by water involves formation of corrosion products (especially $Fe(OH)_3$) that can occlude the pores of the reactive medium causing permeability reduction. These reactions, according to permeability profiles, seem favoured when the initial Ni concentration in input into the column decreases. The reason could be related to a possible competition between the possible reducing agents (the water and the contaminant) toward iron oxidation.

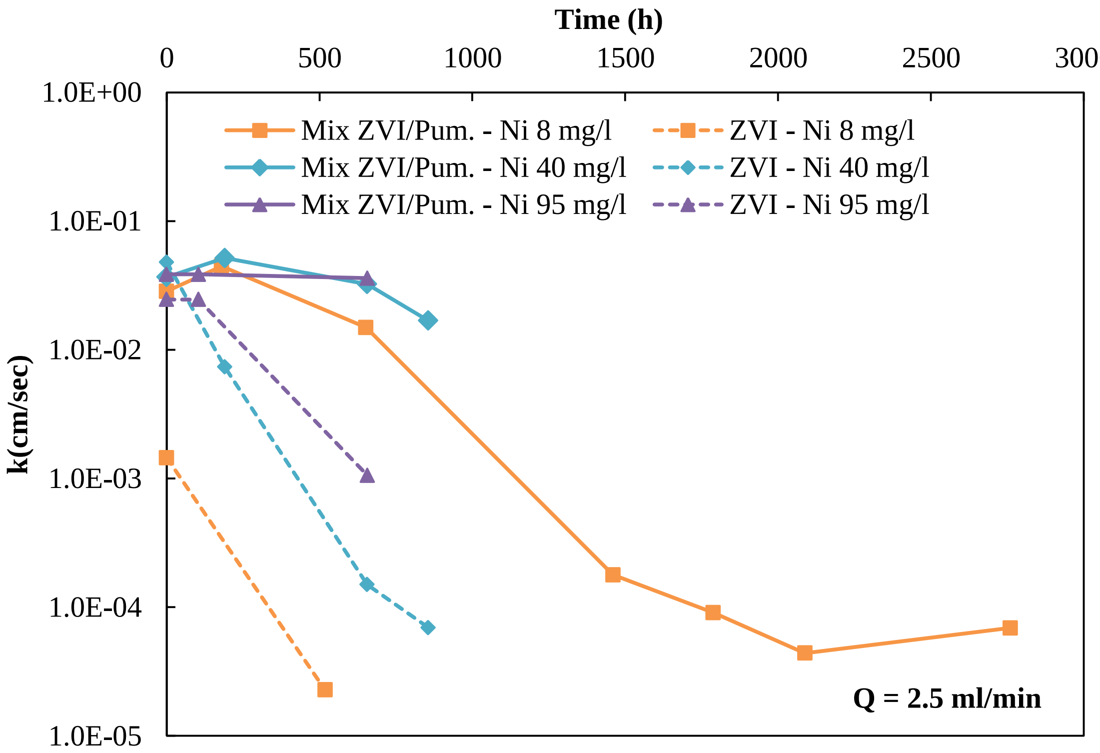


Figure 7-14Hydraulic conductivity vs. time for column tests carried out at different values of initial nickel concentration

7.3. 3 Release of iron during column tests

During column tests measurements of iron concentration in the solution samples withdrawn at the outlet of the column were carried out.

Figure 7-15 shows the values of iron concentration measured during the column tests carried out at flow rate of 2.5 ml/min and using an initial contaminant concentration of 8 and 40 mg/l as function of contaminant mass in input into the column using a semi-logarithm scale. The values of iron released by the reactive media tested are always below the limit concentration allowed in groundwater by Italian regulation (D. Lgs. 152/2006) and equal to 0.2 mg/l at the begging of the tests or when the reactivity of the medium is maximum and the contaminant is easily removed. Iron concentration tends to increase with the time in particular when the reactive medium starts to lose its reactivity. The best performance in term of iron release is shown by the mixture between ZVI and Pumice when Nickel is present with an initial concentration of 8 mg/l. The comparison between the mixture and the pure ZVI is not possible due to the different ZVI mass present in the columns. Considering the column tests having an input solution of nickel at initial concentration equal to 40 mg/l the better performance of the mixture than that of ZVI is probably due to the lower content of ZVI present in the mixture.

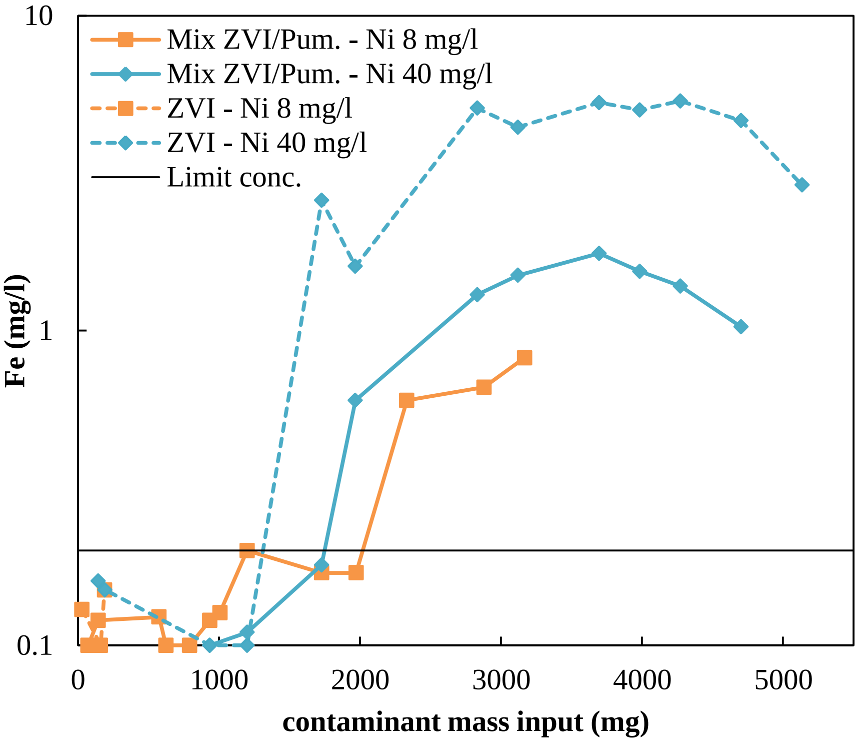


Figure 7-15 Iron concentration (mg/l) measured at the outlet of the column as function of contaminant mass in input (semi-logarithm scale)

7.4 Effect of flow rate

In order to study the effect of flow rate on the efficiency of ZVI and of the granular mixture ZVI/Pumice, column tests using different values of flow rate were carried out. The flow rate effects were studied using a nickel solution at initial concentration of 40 mg/l and three different values of flow rate (i.e. 0.1, 0.5 and 2.5 ml/min), whereas using a copper solution at initial concentration of 500 mg/l, two different values of flow rate (i.e. 0.1, 0.5 ml/min) were used.

The flow rates 0.1, 0.5 and 2.5 ml/ml correspond to a Darcy velocity of 0.07, 0.38 and 1.9 m/day respectively.

Figure 7-16 and Figure 7-17 show the Ni breakthrough curve at different sampling ports versus time in the ZVI/Pumice for the column tests carried out at 0.1 ml/min and 0.5 ml/min respectively.

The column test carried out using the lowest flow rate shows a good performance in term of removal capacity in fact Ni concentration at sampling port located at 50 cm is maintained below 1 mg/l over a long period (404 days or 145 PV). When a flow rate of 0.5 ml/min is used, Ni concentration measured at the outlet of the columns increases more rapidly and a value of 1 mg/l is exceeded already after 120 h or 8.9 PV.

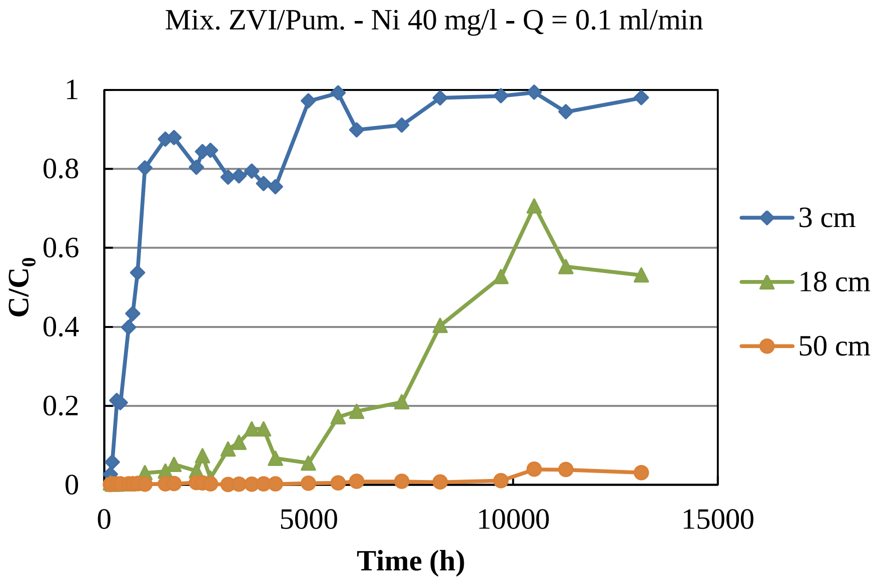


Figure 7-16 Ni breakthrough curve at different sampling ports versus time in the mixture ZVI/Pum. (Q=0.1 ml/min)

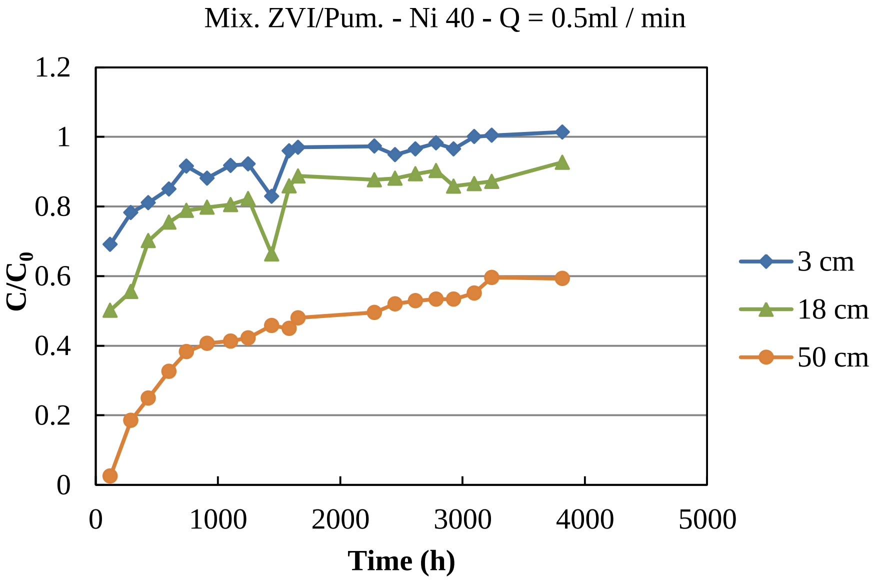


Figure 7-17 Ni breakthrough curve at different sampling ports versus time in the mixture ZVI/Pum. (Q=0.5 ml/min)

Figure 7-18 and Figure 7-19 show the Ni breakthrough curve at different sampling ports versus time in the ZVI for the column tests carried out at 0.1 ml/min and 0.5 ml/min respectively. Using the lowest nickel concentration, the metal in the first sampling port (3 cm) reveals a relative concentration of about 0.1 (Figure 7-18) for all duration of the test, interrupted due to a decrease of hydraulic conductivity of three order of magnitude.

When a flow rate of 0.5 ml/min is used, the relative concentration (C/C_0) is always above 0.5 (Figure 7-19).

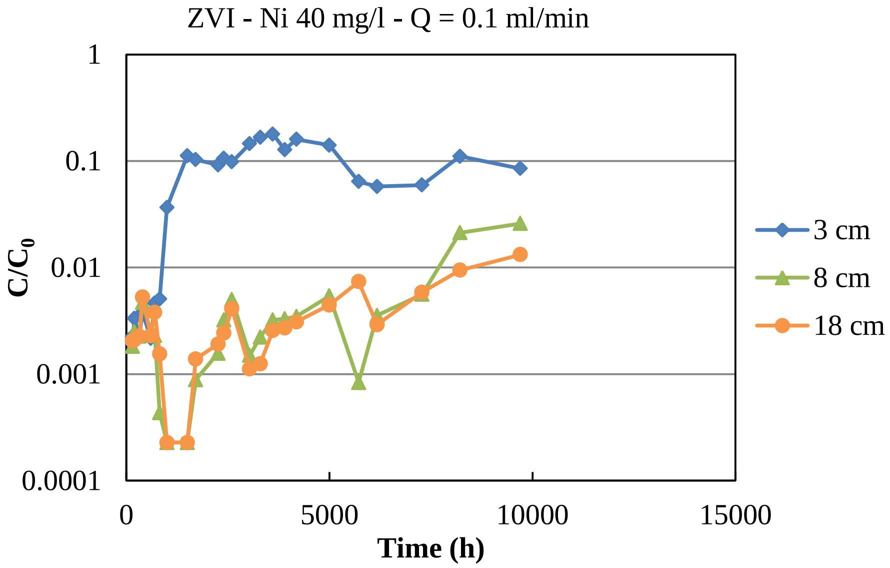


Figure 7-18 Ni breakthrough curve at different sampling ports versus time in ZVI (Q=0.1ml/min)

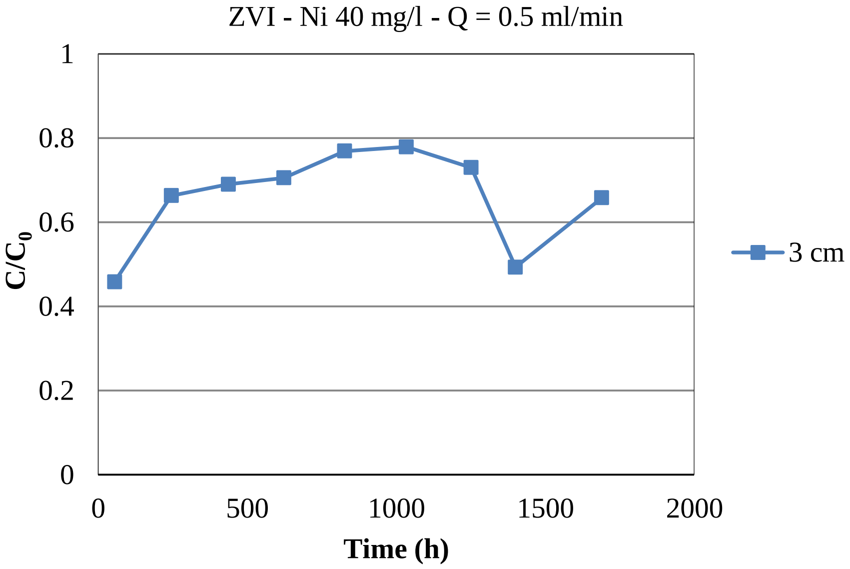


Figure 7-19 Ni breakthrough curve at outlet versus time in ZVI (Q=0.5ml/min)

In the column tests carried out using a copper solution and a flow rate of 0.5 ml/min the contaminant is removed from solution with a concentration measured at the outlet being below the limit concentration allowed by Italian regulation (D. Lgs. 152/2006).

In the column test carried out using the mixture ZVI/Pumice and the lowest value of flow rate, the contaminant mass flowed into the column was greater than that flowed in the same reactive medium but using an higher flow rate. In this case an exhaustion of the reactive medium was observed as Figure 7-20 shows where copper concentration along column distance is plotted for different sampling time.

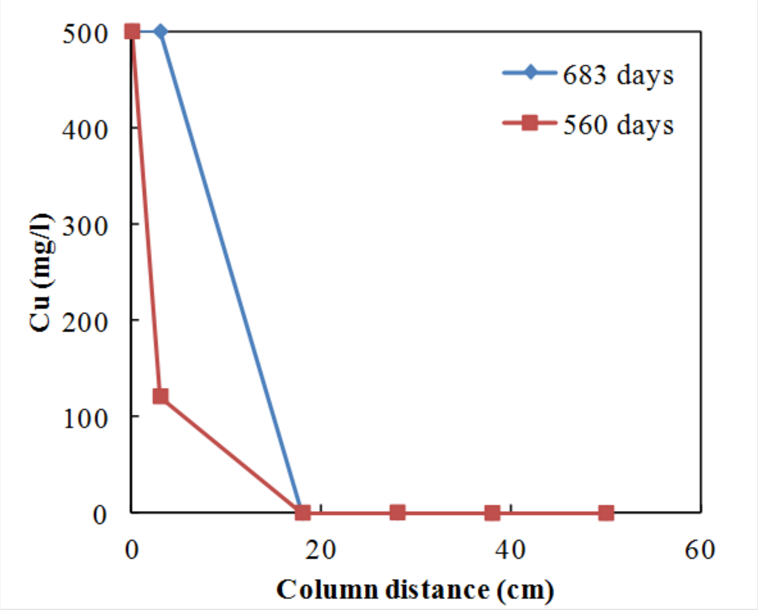


Figure 7-20 Copper concentration (mg/l) along column distance for different sampling time

In the column test carried out using the lowest flow rate and the only ZVI an exhaustion of the reactive medium was not observed for all the duration of the test which, unlike the mixture, was forcedly interrupted because of column clogging.

7.4.1 Effect of flow rate on nickel removal

Figure 7-21 and Figure 7-22 illustrate the influence of flow rate on contaminant removal showing the nickel mass discharged from the outlet of the column as a function of the nickel mass in input, the latest figure refers to the first 1200 mg of nickel flowed into the column for a better visualization of results. The output of column tests where 1680 gr of ZVI were used, was considered at 3 cm of column length.

The best performance in term of removal capacity between column tests where a granular mixture of ZVI/Pumice was used (Figure 7-21), is registered by the column tests carried out with the lowest flow rate. This behaviour can be easily explained by the longer residence time. In particular, the pollutant was almost completely removed at the lowest flow rate, while breakthrough occurred earlier and removal was significantly reduced at higher flow rates. These results are in good agreement with those reported by Komnitsas et al. 2007 and Prasad et al.

2011. Column tests carried out with ZVI (Figure 7-22) show the bests performance for the column where the lowest flow rate was used.

In Figure 7-21 and Figure 7-22 the removal capacity of the two reactive media tested can be compared since the same amount of ZVI is considered. For all values of flow rates used the ZVI/pumice mixture shows a better performance than ZVI only. These results clearly confirm another time that using the ZVI/pumice mixture is beneficial, since increased residence time enhances the sorption process and promotes contaminant removal (Moraci and Calabrò, 2010).

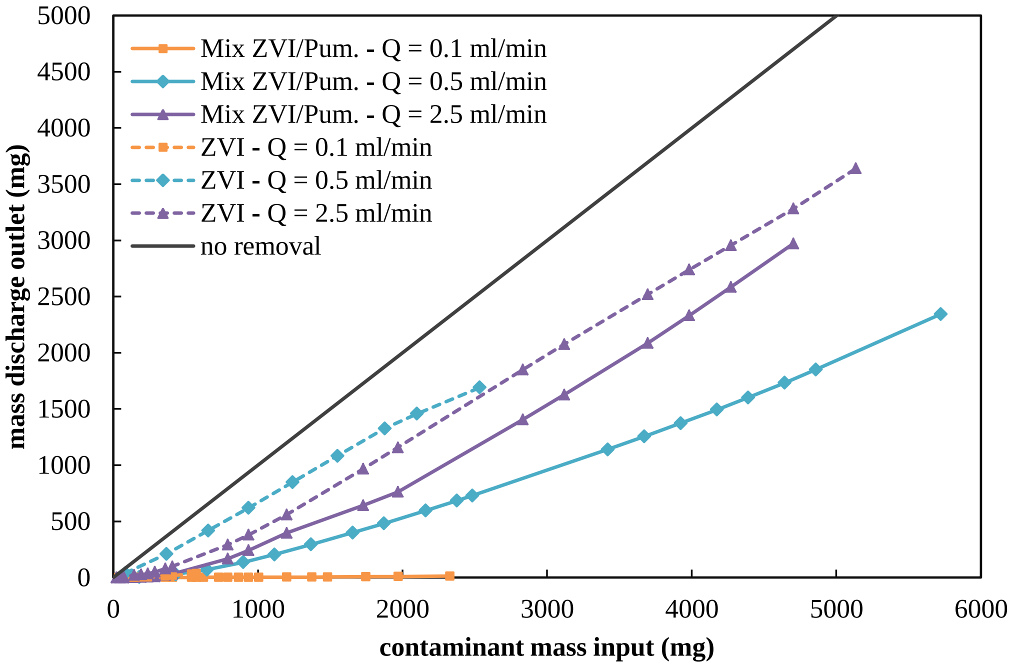


Figure 7-21 Nickel mass discharge from the outlet of columns vs. nickel mass in input for column tests carried out under different values of flow rates

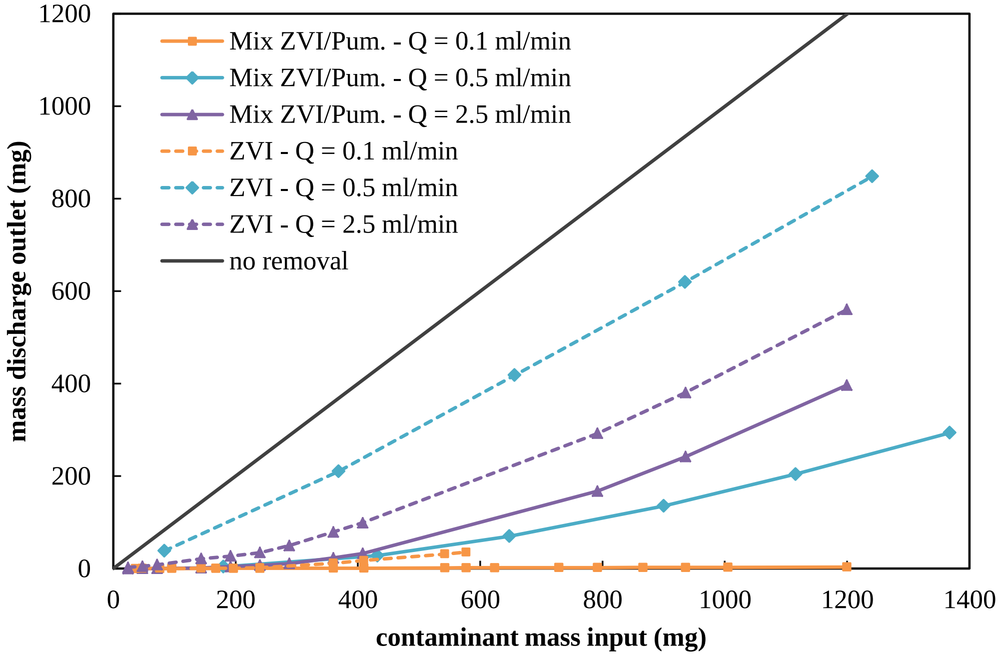


Figure 7-22 Nickel mass discharge from the outlet of columns vs. nickel mass in input for column tests carried out under different values of flow rates (for the first 1200 mg of nickel flowed into the column).

In order to characterize the capability of tested materials for contaminant removal, the specific removal capacity related to ZVI only (SRC_{ZVI}) was calculated using eq. 22 (Chapter 5). The specific removal referred to all mass of ZVI present into the column (SRC_{ZVI}) and referred to only 240 gr ($SRC_{ZVI(240\ gr)}$), were calculated (Table 7-4).

Table 7-4 Specific removal capacity (Effect of flow rate)

Flow rate [mL/min]	Reactive medium	Ni flowed [g]	SRC_{ZVI} [mg/g]	$SRC_{ZVI\ (240\ gr)}$ [mg/g]
0.1	ZVI/Pum.	1.75	$7.22 \cdot 10^{-3}$	$7.22 \cdot 10^{-3}$
0.5	ZVI/Pum.	2.54	$7.25 \cdot 10^{-3}$	$7.25 \cdot 10^{-3}$
2.5	ZVI/Pum.	4.70	$7.15 \cdot 10^{-3}$	$7.15 \cdot 10^{-3}$
0.1	ZVI	1.75	$1.11 \cdot 10^{-3}$	$6.02 \cdot 10^{-3}$
0.5	ZVI	2.54	$3.50 \cdot 10^{-3}$	$3.50 \cdot 10^{-3}$
2.5	ZVI	4.70	$2.28 \cdot 10^{-3}$	$6.28 \cdot 10^{-3}$

The values of SRC_{ZVI} and the $SRC_{ZVI(240\ gr)}$ for the ZVI/pumice are higher than those calculated for ZVI, demonstrating the positive effect of pumice in improving the removal capacity of ZVI as previously mentioned in § 7.3. 1.

7.4.2 Effect of flow rate on copper removal

Column tests carried out using an initial copper concentration of 500 mg/l and two different values of flow rates (i.e. 0.1 – 0.5 ml/min) allow to evaluate the effect of flow rate on the performance of the reactive media tested (the mixture ZVI and Pumice at weight ratio 30:70 and the pure ZVI). Considering the same contaminant mass flowed into the column and considering the duration of the test carried out at flow rate of 0.5 ml/min the two media are not influenced by the flow rate in term of contaminant removal because copper is always removed from solution and its concentration is below limit concentration allowed by Italian regulation (D. Lgs. 152/2006) and equal to 1 mg/l.

7.4.3 Effect of flow rate on hydraulic conductivity

Determinations of hydraulic conductivity were carried out during the column tests in order to investigate the relative performance of the ZVI/pumice mixture and ZVI alone in terms of permeability. Figure 7-23 and Figure 7-24 show the hydraulic conductivity profile with respect to contaminant mass measured at the input of the column and as a function of time for all of the tests where a solution contaminated by nickel with an initial concentration of 40 mg/l was used.

A first comparison between the two reactive media reveals that the ZVI/pumice mixture is able to maintain the permeability for a longer period than ZVI, ensuring better long-term performance of the permeable barrier. At the lowest flow rate (0.1 ml/min), a permeability decline of three orders of magnitude was observed for the mixture ZVI/Pumice and of five orders of magnitude for ZVI alone. For column tests carried out at a flow rate of either 0.5 ml/min or 2.5 ml/min, for both reactive media, the reduction of the hydraulic conductivity was rather slow. In particular, hydraulic conductivity was almost constant for the whole duration of the tests performed at 0.5 ml/min and for the test carried out at 2.5 ml/min using the ZVI/Pumice granular mixture while for the same test performed using ZVI only a reduction of hydraulic conductivity of less than three order of magnitude was observed only after the flow of about 5 g of nickel in the column. This behaviour could be attributed to a more effective dragging of corrosion products from the pores of the column due to higher flow. Moreover, the comparison of the hydraulic conductivity between tests carried out using the lowest and the highest flow rate indicates that accelerated column tests are not representative of the actual long-term permeability loss of the medium. As already mentioned, a higher flow rate can cause dragging of precipitates that would instead be deposited and clog the medium at lower flow rates.

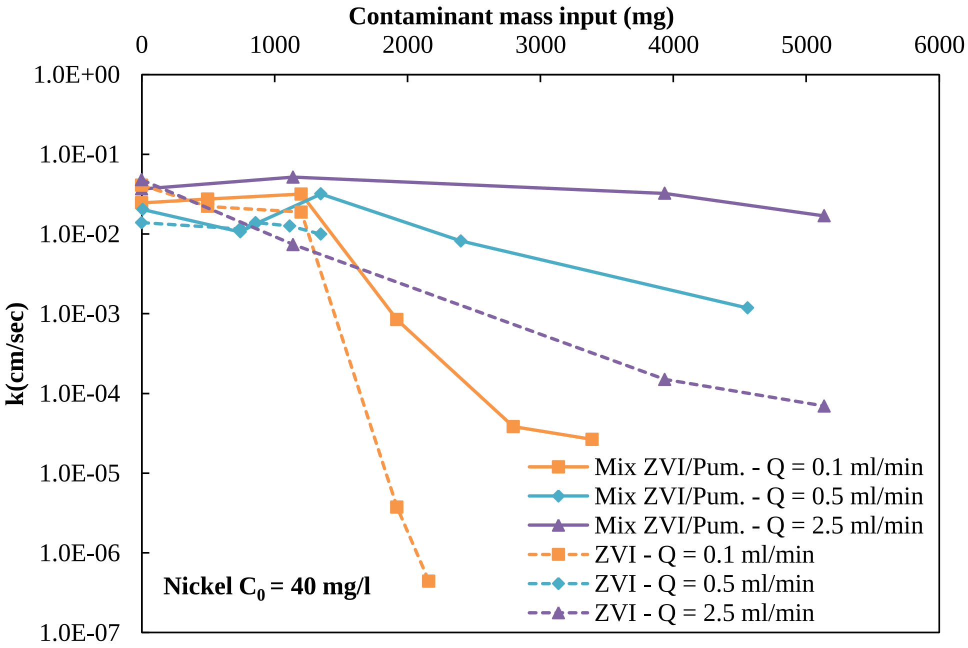


Figure 7-23 Hydraulic conductivity vs. contaminant mass input for column tests carried out at different values of flow rates and using solution contaminated by nickel

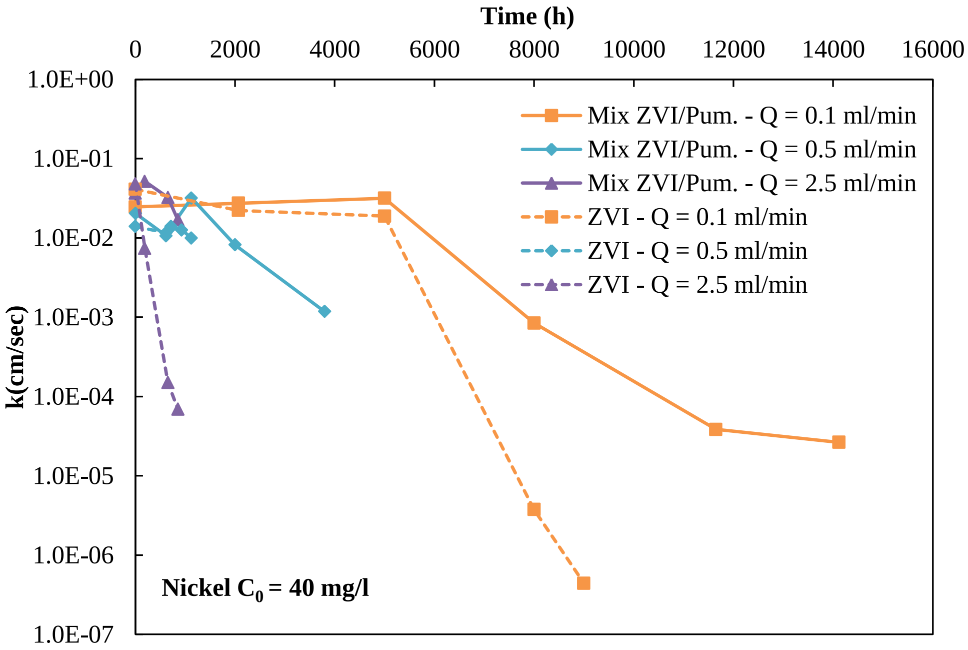


Figure 7-24 Hydraulic conductivity vs. time. for column tests carried out at different values of flow rates and using nickel solution

Column tests carried out using ZVI alone reveal a loss of permeability with time, except for the test in which a lower quantity of ZVI was used. In this test the removal efficiency was lower and the formation of iron corrosion products (especially $Fe(OH)_3$) due to anaerobic oxidation of iron by water was probably limited by the presence of nickel. For this reason a possible competition between the contaminant and the water as potential oxidizing agents may be considered to better explain the results. Therefore, using an amount of reactive medium substantially greater than that required for contaminant removal may be unfavourable for PRB design since the iron not used for contaminant remediation may be oxidized by water, leading to faster clogging of the barrier.

When column tests carried out using a solution contaminated by copper are considered, the effect of flow rate on permeability is rather different compared to that observed with a solution contaminated by nickel. When the same amount of contaminant in input into the columns is considered, permeability reduction occurs firstly in the column test carried out with ZVI alone and using a flow rate of 0.5 ml/min (Figure 7-25).

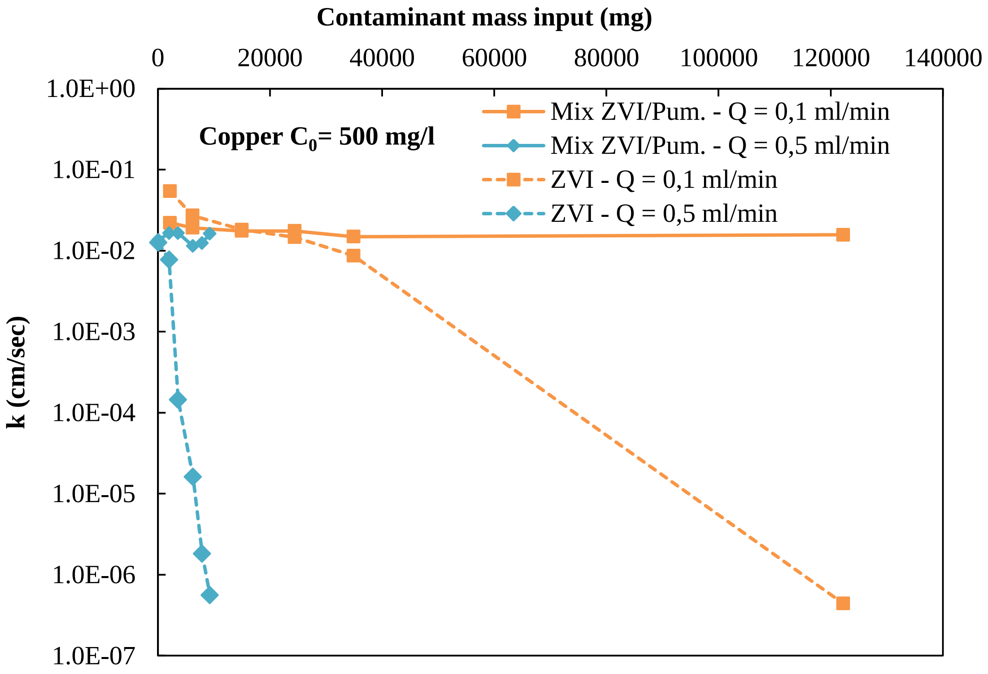


Figure 7-25 Hydraulic conductivity vs. contaminant mass input for column tests carried out at different values of flow rates and using copper solution

This behaviour could be due to the presence of nitrate (the contaminant solution is in fact prepared using copper nitrate) and to the different removal mechanism between nickel and copper. A copper concentration equal to 500 mg/l implies a concentration of nitrate equal to 1000 mg/l that can influence the behaviour of the ZVI. As showed in literature, nitrate contribute to increase iron surface passivation and decrease rates of iron corrosion (Farrel et al., 2000). In the column test carried out using a low flow rate the contribution of nitrate to iron passivation is probably favoured by the longer residence time, a passivation of iron implies a reduced formation of expansive corrosion products responsible for column clogging.

The mixture of ZVI and pumice is able to maintain a constant permeability respect to the use of ZVI alone in both conditions of flow rate (Figure 7-25).

7.5 Column tests acceleration through flow rate or contaminant concentration increase

Column tests can be accelerated by increasing the mass of contaminant in input into the column. This increase can be achieved using higher values of flow rate or initial contaminant concentration. In this section is investigated the effect of an increase of contaminant concentration or flow rate on the results of column tests. In particular it is evaluated if an increase in contaminant concentration produces the same effect of an increase in flow rate on the reactive medium behaviour.

Therefore, in this chapter are put in comparison the results of column tests carried out using the mixture ZVI/Pumice and different values of flow rates and nickel concentration. Figure 7-26 and Figure 7-27 show Nickel mass discharge from the outlet of columns as function of respectively nickel mass in input into the column and time (h).

If a flow rate of 0.1 ml/min, which corresponds to a Darcy velocity of 0.07 m/day, is representative of in situ condition the acceleration of the column test through the flow rate implies an underestimation of the removal capacity of the medium. If the lowest nickel concentration used in the test is representative of in situ concentration, the acceleration of the column test by means of contaminant concentration implies an underestimation of the removal capacity of the medium. Accelerated column tests by means of un increase of the flow rate or of the contaminant concentration can be a safe procedure to determine the removal capacity of the medium but this is not the case when evaluating long-term permeability, which is a key factor in ensuring the correct operation of a permeable reactive barrier. In fact, column tests accelerated through flow rate or contaminant concentration do not reproduce the real medium permeability loss as showed in Figure 7-28 where permeability profile is plotted as function of contaminant mass input.

A similitude of results, in term of removal capacity (Figure 7-26 and Figure 7-27) and permeability, can be observed for the tests where the flow rate differs of 25 times and nickel concentration of 5 times (i.e. column test carried out using a flow rate of 0.1 ml/min and Ni concentration equal to 40 mg/l and the column test carried out with a flow rate of 2.5 ml/min and Ni concentration equal to 8 mg/l).

Obviously a column test carried out using the highest flow rate implies a significant reduction of test duration (2000 h against 8000 h).

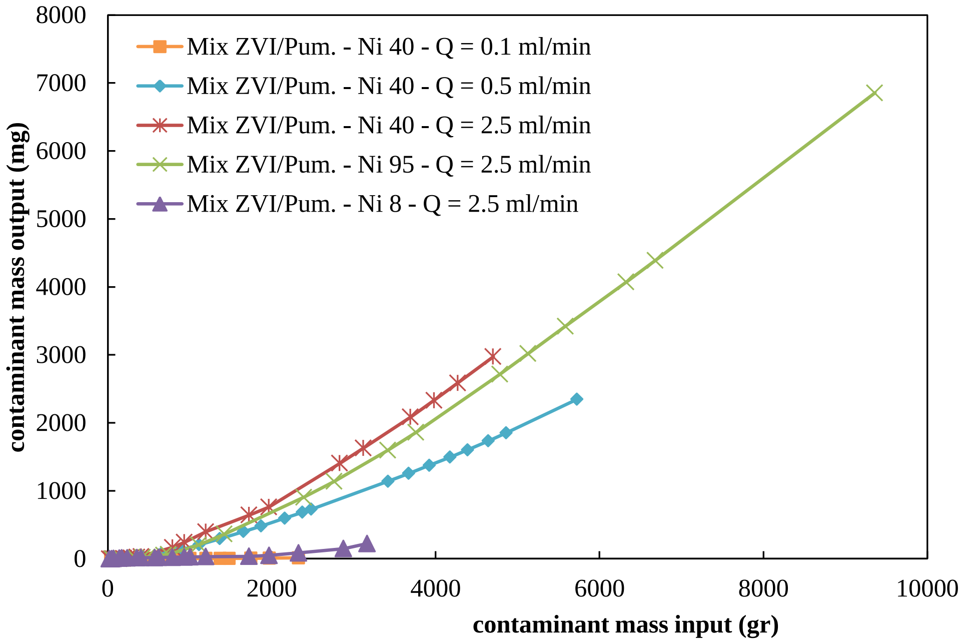


Figure 7-26 Nickel mass discharge from the outlet of columns vs. nickel mass in input for column tests accelerated through contaminant concentration or flow rate.

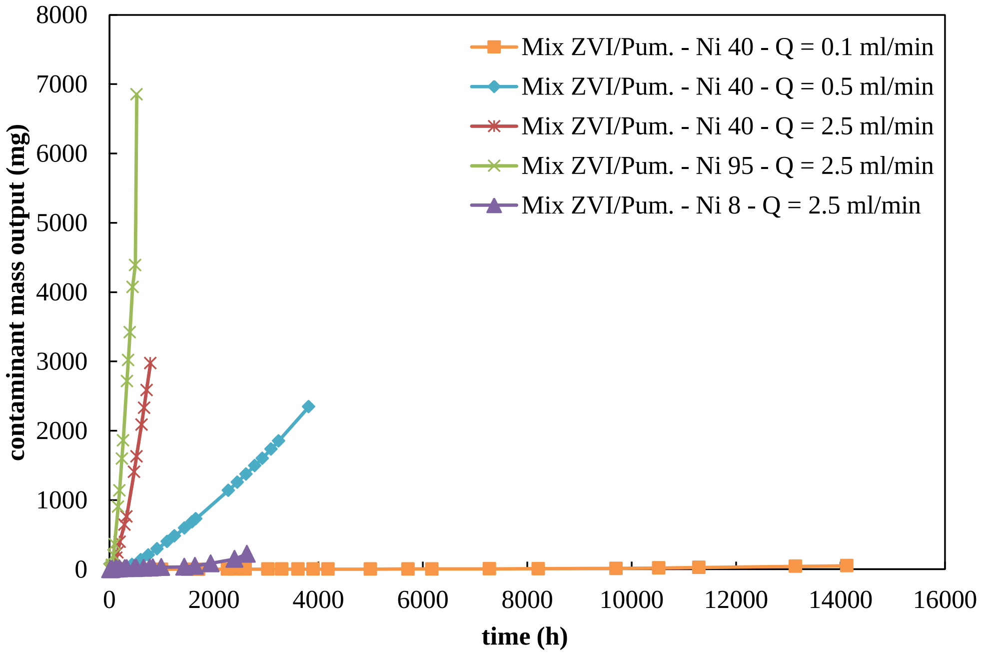


Figure 7-27 Nickel mass discharge from the outlet of columns vs. time for column tests accelerated through contaminant concentration or flow rate

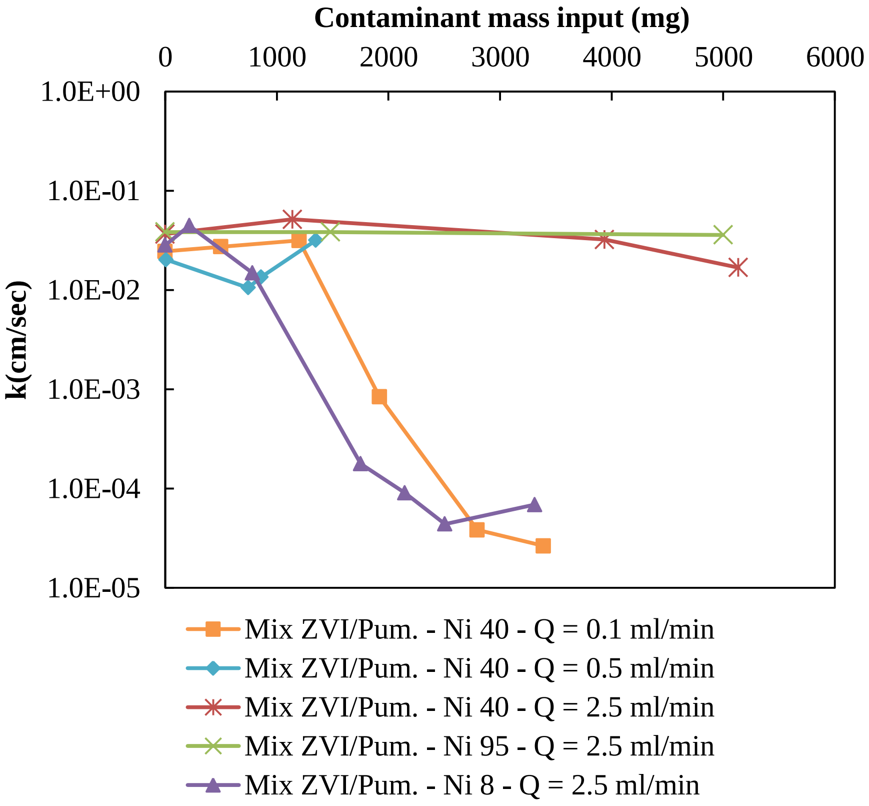


Figure 7-28 Hydraulic conductivity vs. contaminant mass input for column tests accelerated through contaminant concentration or flow rate

7.6 Kinetic interpretation of column tests

The design of a PRB implies the knowledge of the kinetic rate constant as described in § 2.3.5.1. Therefore an attempt to interpret column tests results through a first-order kinetics was carried out. In order to find the rate constant k, the values of relative concentration calculated at different sampling times were plotted against residence time obtained converting the distances through the column as explained in § 2.3.5.1. The values were interpolated through eq. 1.

The degree of fit was determined by calculating the correlation coefficient (R^2). The R^2 value indicates how well the first-order model fits the experimental data. In literature the first-order kinetics are mostly reported for initial reaction rates, but it should be remembered that the rates are increasingly deviated from the first-order kinetics with increasing time (Melitas and Farrell, 2002; Ponder et al., 2000).

Figure 7-29 shows the interpolation of relative concentration (C/C_0) against residence time (h) through a first-order kinetic. The values refer to the first sampling carried out after 4 h of column test where a mixture of ZVI/Pumice, a flow rate of 2.5 ml/min and an initial Nickel concentration of 40 mg/l is used.

Figure 7-30 shows the rate constant values obtained at different sampling times for the same column tests. The R^2 values decrease in time up to a value of 0.6.

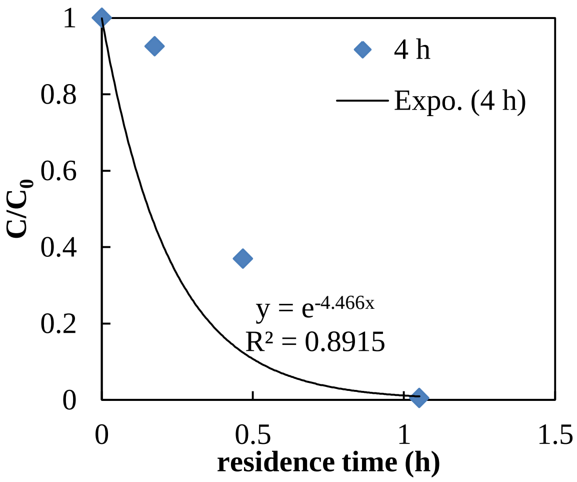


Figure 7-29 C/C_0 vs. residence time (h) calculated after 4 h of column test carried out with the mixture ZVI/Pumice (Q=2.5 ml/min and Nickel C_0=40 mg/l)

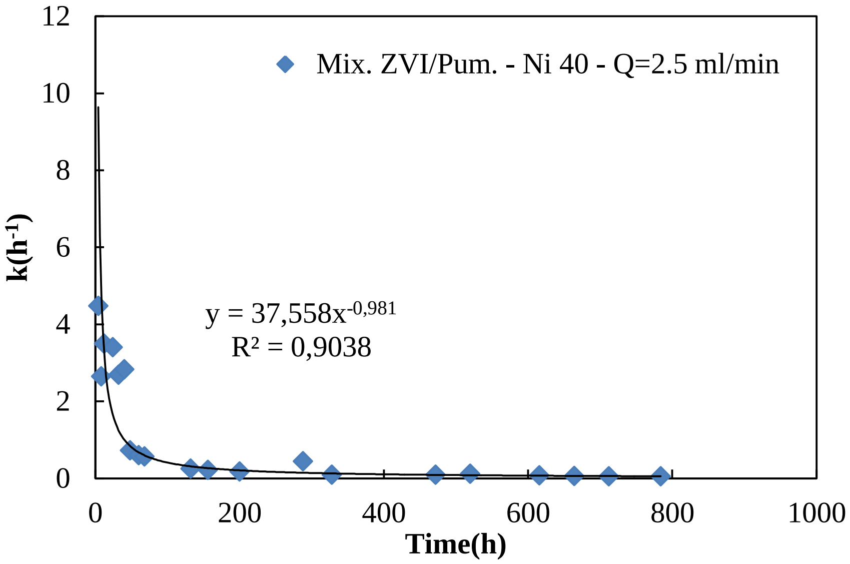


Figure 7-30 Rate constant values obtained for a granular mixture ZVI/Pumice (Q=2.5 ml/min and Nickel C_0=40 mg/l) at different sampling times

The values are fitted with potential function. The results obtained in the same tests conditions but using the only ZVI are best fitted with a first-order kinetic (Figure 7-31) in fact R^2 values are higher than that calculated for the mixture ZVI/Pumice. The Rate constant values obtained for the pure ZVI are higher than that of the mixture and decrease in the time as shown in Figure 7-32. The results are fitted with potential function.

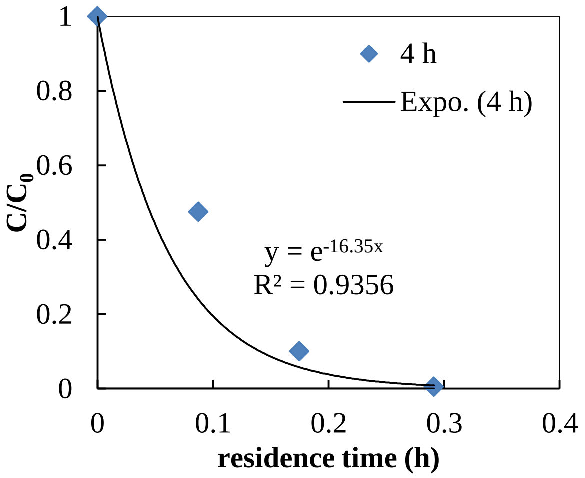


Figure 7-31 C/C_0 vs. residence time (h) calculated after 4 h of column test carried out with the ZVI (Q=2.5 ml/min and Nickel C_0=40 mg/l)

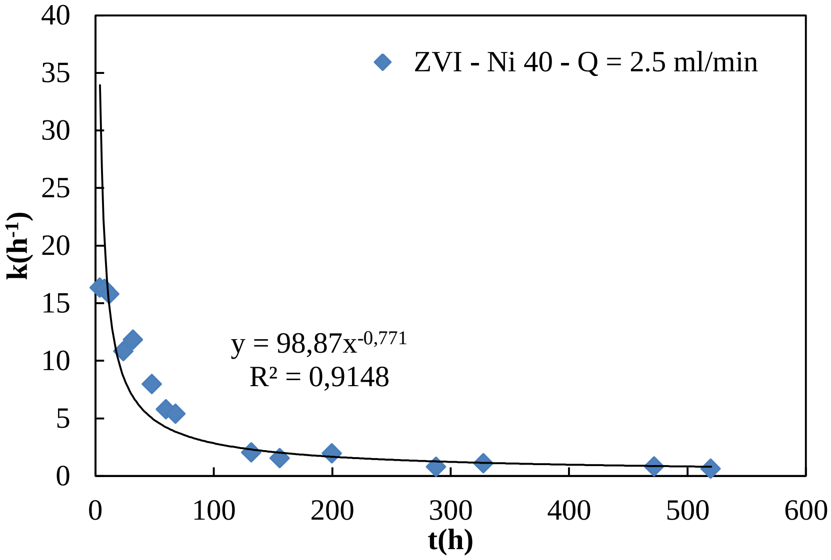


Figure 7-32 Rate constant values obtained for the ZVI (Q=2.5 ml/min and Nickel C_0=40 mg/l) at different sampling times

In Table 7-5 are summarized the values of rate constant k, the sampling time at which k calculation refers, the R^2 value, the potential equation which fits the values of rate constant as function of time sampling and the relative R^2 value.

The rate constant values obtained at different sampling times, for the column test using the mixture ZVI/pumice and a solution contaminated by nickel at initial concentration of 8 mg/l, cannot be fitted with a potential function because values maintains in the range 2-3 for most of the time.

Table 7-5 Rate constant values

Reactive medium	Flow rate (ml/min)/ Ni conc. (mg/l)	k [1/h]	Time [h]	R^2	logarithmic function	R^2
Mix ZVI/Pum.	2.5 – Ni 8	4.902	20	0.86	-	-
Mix ZVI/Pum.	2.5 – Ni 40	4.466	4	0.89	$k = 37.558\ (t)^{-0.981}$	0.90
Mix ZVI/Pum.	2.5 – Ni 95	4.736	4	0.94	$k = 70.591\ (t)^{-1.095}$	0.92
ZVI	2.5 – Ni 8	23.94	20	0.71	NA*	NA*
ZVI	2.5 – Ni 40	16.35	4	0.93	$k = 98.87\ (t)^{-0771}$	0.91
ZVI	2.5 – Ni 95	16.28	4	0.89	$k = 162.04\ (t)^{-0.941}$	0.86
Mix ZVI/Pum.	0.1 – Ni 40	0.481	152	0.8	$k = 6.5569\ (t)^{-0.503}$	0.87

* Not available due to the short duration of the test

7.7 Analyses of the exhausted medium

At the end of the column tests, visible changes in the colour of the reactive medium can be observed. Figure 7-33, Figure 7-34 and Figure 7-35 show the photo taken at the end of column test carried out with ZVI using a flow rate of 2.5 ml/min and solution contaminated by nickel at initial concentration of 95, 40 and 8 mg/l respectively. Different colours from slight reddish (Fe^{3+} hydroxide) to greyish green (Fe^{2+} hydroxide) can be observed near the inlet of the column.

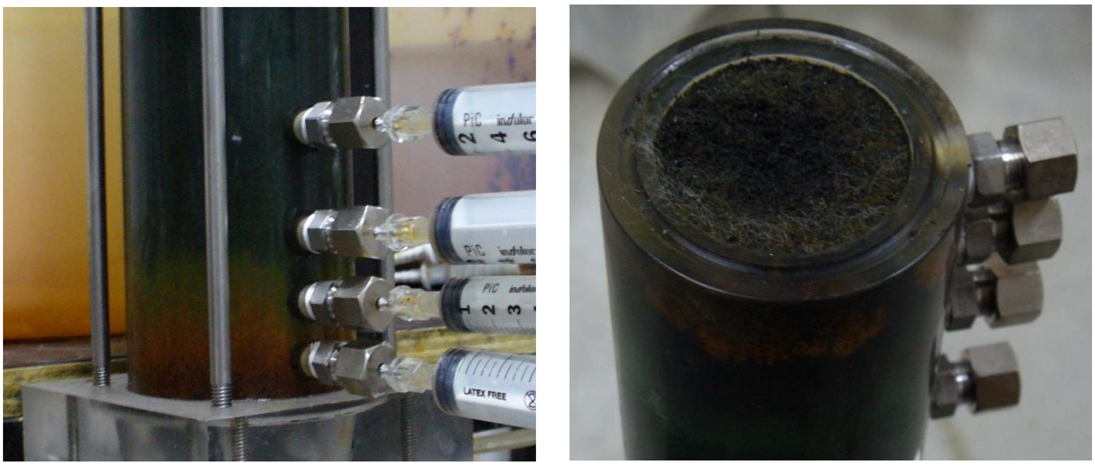


Figure 7-33 Images of the column test carried out with ZVI (Q=2.5 ml/min and Ni 95 mg/l)

Figure 7-34 Images of the column test carried out with ZVI (Q=2.5 ml/min and Ni 40 mg/l)

Figure 7-35 Images of the column test carried out with ZVI (Q=2.5 ml/min and Ni 8 mg/l)

Figure 7-36 Image of the column tests carried out with the mixture ZVI/Pumice (Q=0.1ml/min) and a solution contaminated by nickel (on the left) and copper (on the right).

At the end of some column tests the exhausted reactive medium was withdrawn from column and analysed for investigating the mineral species generated during the contact of the contaminant solution with the reactive material.

Scanning electron microscope (SEM) was used to evaluate the morphology and spatial relationships among mineral precipitates on the surfaces of zero valent iron particles.

According to literature, SEM images of exhausted ZVI exhibit two types of morphology: acicular aggregates and cryptocrystalline clusters (Forukawa et al., 2002). Acicular aggregates are largely composed of green rust minerals, goethite, lepidocrocite, and calcium carbonate phases, whereas cryptocrystalline clusters contained mackinawite and poorly crystallized iron (oxy-) hydroxides (Forukawa e t al., 2002).

The SEM images of ZVI sample (Figure 7-37) withdrawn from the inlet of column after the test carried out at flow rate of 2.5 ml/min and with a solution contaminated by nickel (C_0 = 40 mg/l) shows the presence of needle-like/acicular shape typical of Goethite and the probably presence of Ni_2O_3 whose SEM image is shown in Figure 7-40. SEM images of ZVI sample withdrawn from the inlet of column test carried out at flow rate of 2.5 ml/min and with a solution contaminated by nickel (C_0 = 8 mg/l), seems to show (Figure 7-38) the presence of pseudocubic form of probably magnetite. Finally Figure 7-39 shows SEM images of ZVI sample withdrawn from the inlet of column test carried out at flow rate of 2.5 ml/min and with a solution contaminated by nickel (C_0 = 95 mg/l) and using the mixture ZVI/Pumice, in this case the iron was magnetically separated from Pumice. In this case can be observed the presence of goethite and of Ni_2O_3.

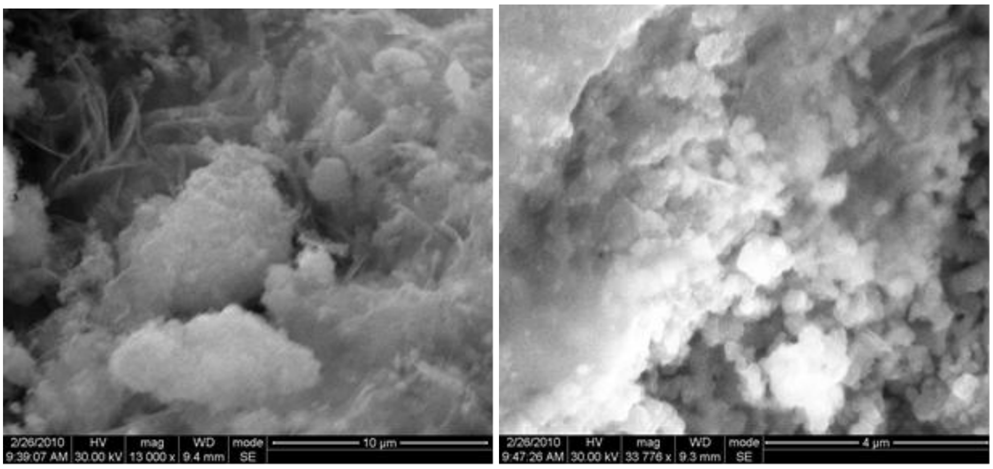


Figure 7-37 SEM images of ZVI sample withdrawn from column test carried out at flow rate of 2.5 ml/min and with a solution contaminated by nickel (C_0 = 40 mg/l)

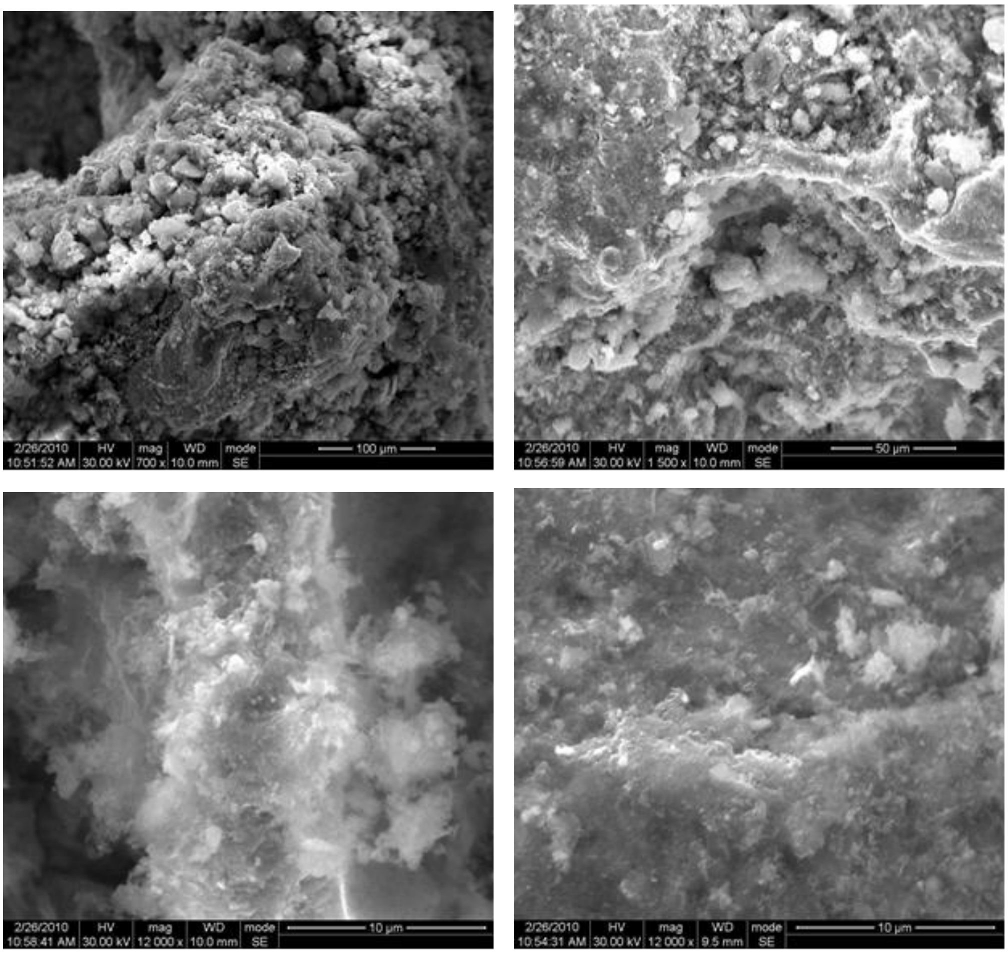


Figure 7-38 SEM images of ZVI sample withdrawn from column test carried out at flow rate of 2.5 ml/min and with a solution contaminated by nickel (C_0 = 8 mg/l)

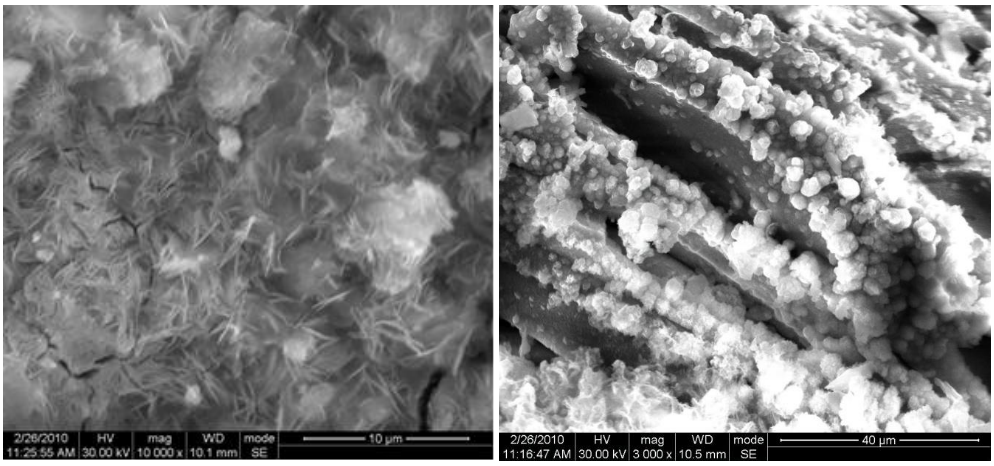


Figure 7-39 SEM images of ZVI sample drawn from column test carried out at flow rate of 2.5 ml/min, with the mixture ZVI/Pumice and a solution contaminated by nickel ($C_0 = 95$ mg/l)

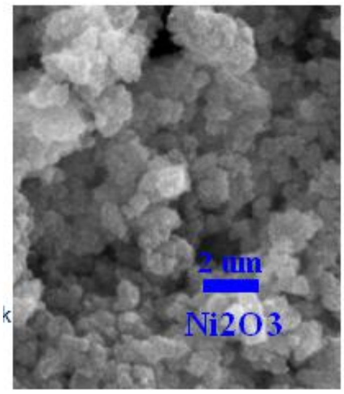


Figure 7-40 SEM image of Ni_20_3

The ZVI withdrawn from the column after the test carried out with a flow rate of 0.1 ml/min and a contaminant solution of nickel at initial concentration of 40 mg/l was analysed by X-ray Photoelectron Spectroscopy (XPS) (I am grateful to CNR-ITAE of Messina). XPS analyses were performed by a Physical Electronics GMBH PHI 5800-01 spectrometer, using a monochromatized Al-Kα radiation on samples withdrawn from the column at three different positions: at the inlet of column (1 cm), at about the middle the medium (8 cm) and near the outlet (18 cm).

The XPS Spectra (Figure 7-41) of ZVI sample withdrawn from 1 cm of column length reveals the presence of Goethite (FeOOH), Hematite (Fe_2O_3) and Magnetite (Fe_3O_4) and the presence (Figure 7-42) of nickel oxides (Ni_2O_3 - NiOH). Atomic concentration is summarized in Table 7-6.

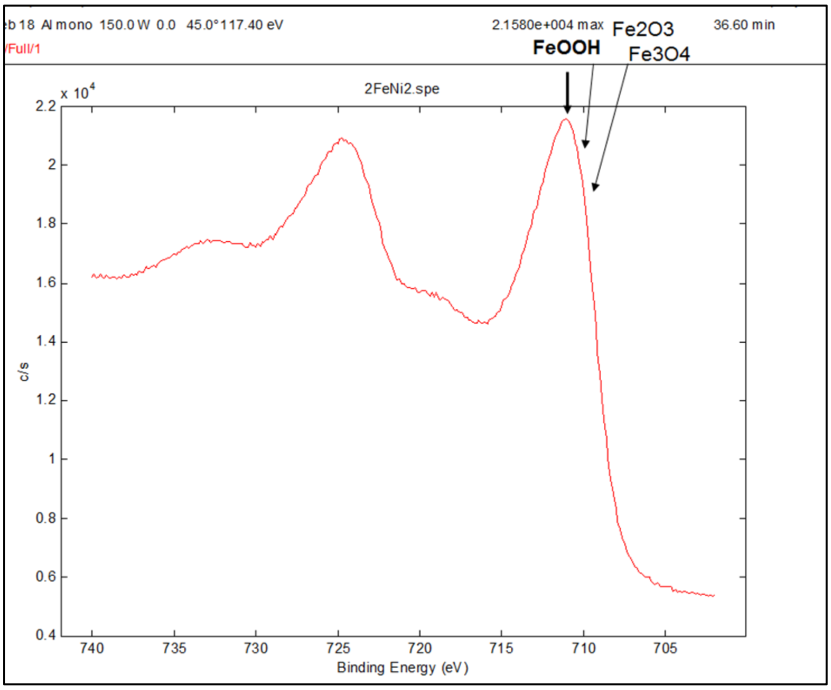


Figure 7-41 XPS spectra of ZVI sample withdrawn from 1 cm of column length

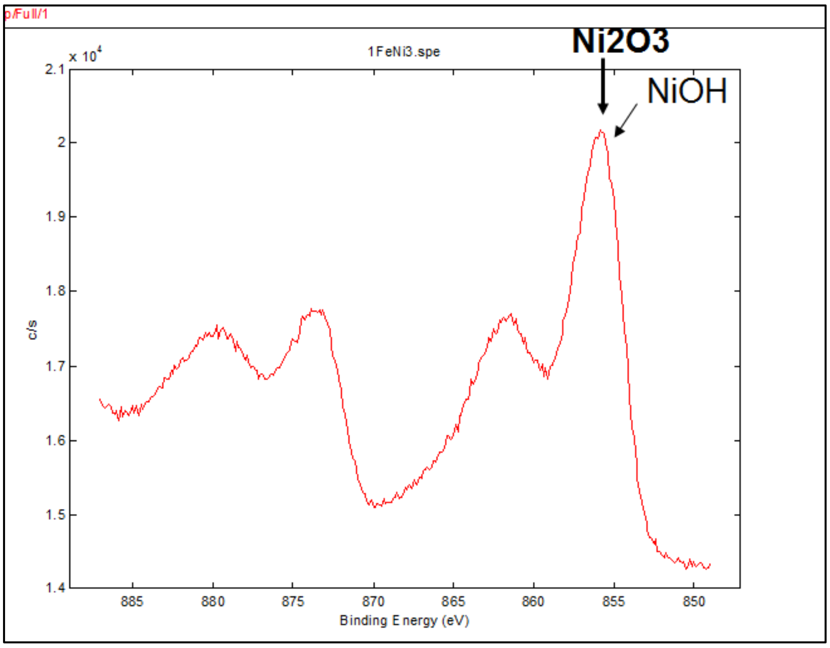


Figure 7-42 XPS spectra of ZVI sample withdrawn from 1 cm of column length

Table 7-6 Atomic concentration of sample withdrawn from 1 cm of column length

C1s	O1s	Fe2p3	Ni2p3
[0.314]	[0.733]	[1.964]	[2.309]
18.42	58.70	12.67	10.22

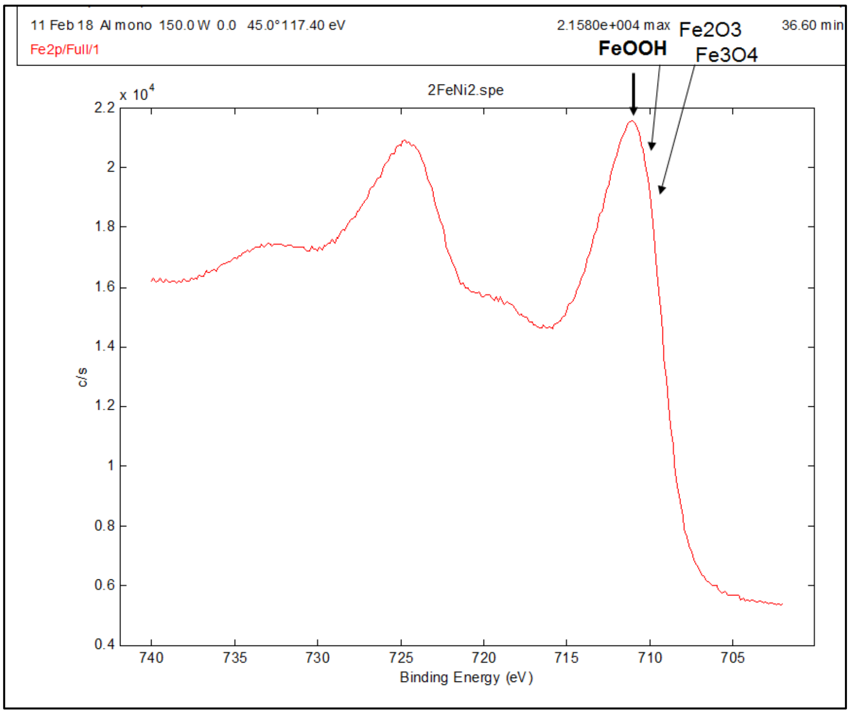


Figure 7-43 XPS spectra of ZVI sample withdrawn from 8 cm of column length

Table 7-7 Atomic concentration of sample withdrawn from 8 cm of column length

C1s	O1s	Na1s	Mn2p3	Fe2p3	Ni2p3
[0.314]	[0.733]	[1.102]	[1.757]	[1.964]	[2.309]
30.40	50.48	1.12	1.30	15.73	0.02

The XPS Spectra (Figure 7-43) of ZVI sample withdrawn from 8 cm of column length reveals the presence of Goethite (FeOOH), Hematite (Fe_2O_3) and Magnetite (Fe_3O_4) and the presence of Nickel is negligible. Atomic concentration is summarized in Table 7-7 and shows a greater concentration of C, O and Fe than the atomic concentration of sample withdrawn from 1 cm of column length.

The XPS Spectra (Figure 7-44) of ZVI sample withdrawn from 18 cm of column length reveals the presence of Goethite (FeOOH), Hematite (Fe_2O_3) and Magnetite (Fe_3O_4) and the presence of Nickel is negligible. From atomic concentration (

Table 7-8) can be observed a decrease of C and an increase of O and Fe.

Table 7-8 Atomic concentration of sample withdrawn from 18 cm of column length

C1s	O1s	Fe2p3	Ni2p3
[0.314]	[0.733]	[1.964]	[2.309]
23.86	55.61	20.30	0.04

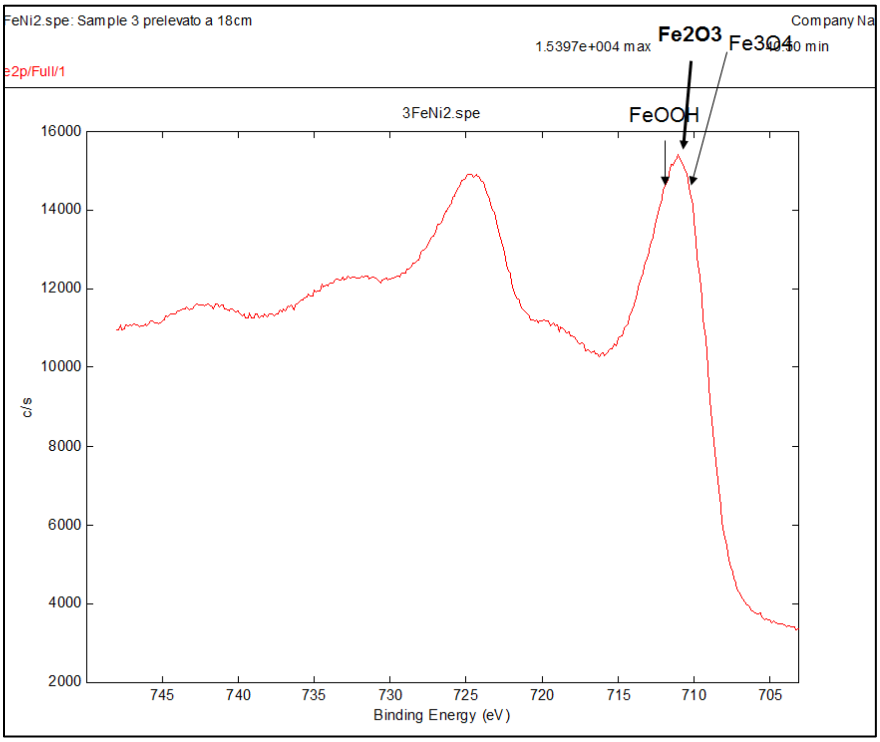


Figure 7-44 XPS spectra of ZVI sample withdrawn from 18 cm of column length

7.8 Conclusions

Column tests analysed in this section were carried out with the aim of studying the behaviour of two reactive media constituted by the pure ZVI and the granular mixture ZVI and pumice at w.r. 30:70 under different conditions of flow rates and contaminant solutions. The flow rate tested were of 0.1 - 0.5 and 2.5 ml/min. Solutions contaminated by copper at concentration of 500 mg/l and of nickel at three different values of concentration (8 – 40 and 95 mg/l) were tested.

The tests allowed to study the following aspects:

1. The effect of initial nickel concentration during experiments carried out at high value of flow rate in order to reach exhaustion of the reactive medium and evaluate its removal capacity;
2. The effect of flow rate for a fixed value of contaminant (nickel and copper) concentration;
3. The acceleration of column tests through the flow rate or the contaminant concentration increase.

Conclusions about the first aspect studied can be summarized as follows:

- The highest removal efficiency for the mixture ZVI/Pumice and for the pure ZVI is registered when the lowest initial nickel concentration (i.e. 8 mg/l) is used;

- Using a higher contaminant concentration of Ni (i.e. 40 mg/l and 95 mg/l) the removal efficiency of both media is almost similar and slightly better for the highest concentration;
- A comparison between the mixture ZVI/Pumice and the pure ZVI, when the same amount of ZVI is considered, confirms the better performance of the mixture. This behaviour is due to the longer residence time guaranteed by the mixture respect to ZVI which is extremely important for nickel removal.
- If the two reactive media tested are compared in term of specific removal efficiency (SRC_{ZVI}) (i.e. mass of contaminant removed respect to ZVI mass) the higher values of this index registered for the mixture demonstrate the positive effect of the pumice in maintaining and improving the typical removal capacity of ZVI.
- In term of permeability, for the reactive media tested, a greater permeability decline can be observed when the lowest value of Ni concentration is used. The reason could be related to a possible competition between the reducing agents (water and the contaminant). Oxidation of ZVI by water, probably more favoured in presence of a lower Ni concentration, implies the formation of corrosion products (especially $Fe(OH)_3$) that can occlude the pores of the reactive medium causing permeability reduction.
- Comparing the behaviour of the two reactive media tested in term of permeability, the mixture in all cases shows its capacity in maintaining for a period longer than ZVI the permeability.
- During some of the column tests carried out using different values of Nickel concentration, the possible release of Fe at the outlet of columns, derived from iron corrosion, was measured. It was observed an increase of iron concentration that can exceed limit value given by Italian Regulation (i.e. 0.2 mg/l) when the reactive medium starts to lose its reactivity (breakthrough).

Conclusions about the second aspect studied can be summarized as follows:

- The best performance in term of removal capacity toward a solution contaminated by nickel is registered in the column tests carried out with the lowest flow rate for both reactive media. This behaviour can be easily explained by the longer residence time.
- For all values of flow rates used the ZVI/pumice mixture shows a better removal efficiency than ZVI. These results additionally confirm that using the ZVI/pumice mixture is beneficial, since increased residence time enhances the sorption process and promotes contaminant removal.
- Regarding solutions contaminated by copper both reactive media tested do not seem influenced by the flow rate in term of contaminant removal because copper is always

removed from solution and its concentration is below limit concentration allowed by Italian regulation (i.e. 1 mg/l).

- Considering the same mass of Ni flowed into the column the greatest loss of permeability is observed for the column tests carried out using the lowest value of flow rate. In condition of low flow rate the precipitation is probably more favoured while using higher flow rates a possible dragging of corrosion products from the pores of the column can be considered.
- Considering the same mass of Cu flowed into the column the effect of flow rate on permeability is rather different compared to that observed with a solution contaminated by nickel. Permeability reduction occurs firstly in the column containing ZVI alone and using a flow rate of 0.5 ml/min. This behaviour could be linked to the different removal mechanisms between nickel and copper.
- In both contaminant solutions the mixture shows its ability to maintain permeability for a longer period than ZVI.

Conclusions about the third aspect studied can be summarized as follows:

- If the lowest flow rate and contaminant concentration are used, the test is considered representative of field condition, it can be stated that, a column test accelerated increasing the flow rate or the contaminant concentration underestimates removal efficiency which can be considered a safe procedure in term of PRB design but it is not able to represent the real permeability loss of the medium.
- Evaluating the behaviour of the reactive medium in terms of both removal efficiency and permeability is necessary for successful barrier design. The behaviour of the reactive medium in the long term may be predicted only through column tests carried out under conditions simulating field conditions as closely as possible. Results obtained over a reasonable time (e.g. 1 year) are useful for PRB design, but the column tests should be prolonged to anticipate eventual hydraulic failure or major reactivity loss in the actual PRB.
- It was evaluated if the results of column tests carried out increasing the flow rate and decreasing contaminant concentration can be compared in term of hydraulic conductivity and removal efficiency with those carried out simulating field condition. A similitude of results is observed between column tests where the flow rate differs of 25 times and contaminant concentration of 5 times (i.e. column test carried out using a flow rate of 0.1 ml/min and Ni concentration equal to 40 mg/l and the column test carried out with a flow rate of 2.5 ml/min and Ni concentration equal to 8 mg/l).

8. COLUMN TESTS: THREE-CONTAMINANTS SOLUTIONS

8.1 Introduction

The use of ZVI in a PRB for the removal of dissolved metals has been studied in literature, in particular, to remove metals from groundwater impacted by mine drainage (Blowes et al., 1998; Blowes et al., 2000; Wilkin et al., 2003; Fiore and Zanetti, 2009; Shokes et al., 1999). Among heavy metals, ZVI was tested, in particular, for redox-sensitive metals such as hexavalent chromium (e.g. Puls et al., 1999; Blowes et al., 1997; Wilkin et al., 2005), uranium (Noubactep et al. 2005) and metalloids such as arsenic (Bang et al. 2005; Lackovic et al. 2000). From previous researches (Dries et al., 2005; Bartzas et al., 2006; Rangsivek and Jekel, 2005) it is now clear that ZVI can also activate removal mechanisms different from oxidation-reduction allowing the removal of metals that cannot be reduced by ZVI (e.g. Zinc). In fact heavy metals can be removed in ZVI systems through redox reactions, precipitation, and sorption. Reduction may be driven by four different reaction paths: Fe^0 (direct reduction), reduction by aqueous Fe^{II}, reduction by adsorbed or structural Fe^{II}, reduction by molecular (H_2) or atomic (H) hydrogen (Noubactep and Schöner, 2009).

The ZVI and the granular mixture of ZVI/Pumice, as discussed in the previous sections, have shown their ability to remove Copper and Nickel from aqueous solutions individually. Therefore in this section the reactive media were tested for the removal of Zinc and of Copper, Nickel and Zinc present at the same time in three-contaminants solutions. The column tests were carried out with a flow rate of 0.5 ml/min in order to complete the tests in a reasonable time. The reactive media tested were ZVI and the mixture ZVI/Pumice at weigh ratio 30:70. Column tests carried out using single-metal solutions and three-contaminants solutions were compared considering the same column length or barrier thickness. The main objective was to verify the occurrence of phenomena of mutual interaction and/or competition among contaminants.

8.2 Literature studies on Copper, Nickel and Zinc removal by ZVI

Literature presents studies on the use of ZVI to remove Cu from acid mine drainage (Shokes and Möller, 1999; Wilkin and McNeil, 2003; Bartzas et al., 2006), from stormwater runoff (Rangsivek and Jekel, 2005) or from syntetic mono-contaminant solutions (Komnitsas et al., 2007; Moraci and Calabrò ,2010). Copper removal was mainly attributed to cementation process that involve the reduction of the oxidized form of contaminant, Cu^{II}, and subsequent deposition of Cu^0 onto the iron surface (Shokes and Möller, 1999; Komnitsas et al., 2007) but also to adsorption and co-precipitation on iron corrosion products (Wilkin and McNeil 2003).

The experiment aimed at evaluating Nickel removal by ZVI (Dries et al., 2005; Bartzas et al., 2006; Moraci and Calabrò, 2010) underlined that the possibility of a spontaneous electrochemical cementation process between Ni and ZVI is less favoured than in the case of copper, because, the standard redox potential of the couple Ni^{2+}/Ni^0 is only slightly higher than that of Fe^{2+}/Fe^0, consequently quantitative removal has been mainly attributed to adsorption, co-precipitation and adsorptive size-exclusion.

Regarding Zinc, reduction by ZVI is excluded since the standard redox potential of the couple Zn^{2+}/Zn^0 is lower than that of Fe^{2+}/Fe^0 and therefore its removal is due to the other mechanisms activated by ZVI (Dries et al., 2005; Bartzas et al., 2006; Rangsivek and Jekel, 2005). According to literature Zn^{2+} can undergo several surface complexation or adsorption reactions with the functional groups at the ZVI surface, it can form unidentate or bidentate surface complexes, metal–ligand complexes such as hydrolyzed Zn ($ZnOH+$) (Dries et al., 2005).

8.3 Column tests setting

Ten column tests, five with columns containing a granular mixture ZVI/Pumice with a weight ratio 30:70, and five containing pure ZVI, were performed using solutions mono-contaminated by either Cu, Ni or Zn or solutions where the three metals were simultaneously present.

The solutions, used to feed the columns, were obtained by dissolving individually or in combination copper nitrate, nickel nitrate and zinc nitrate in distilled water. The concentration values used for single metal solutions were of 500 mg/l for Copper and 50 mg/l for Nickel and Zinc; for the three-contaminants solutions, the concentration values, were of 500 mg/l and 50 mg/l for Copper and 50 mg/l for Nickel and Zinc. Copper was used with two different concentration values in three-contaminant solutions in order to evaluate the effect of copper concentration on the removal of Nickel and Zinc.

To allow a direct comparison of the two different reactive media the ZVI amount was set at 240 gr. In the columns where ZVI was used alone, since it did not fill all the space available (in fact the reactive layer was of about 3 cm), washed quartz gravel was used as filling material. The main information of column tests are summarized in Table 8-1.

Table 8-1 List of column tests carried out with three-contaminant-solutions

Reactive medium	ZVI (gr)	Pum. (gr)	Contaminant/ Concentration (mg/l)	Test duration [h]
ZVI/pum 30:70	240	560	Cu/500	1694
ZVI/pum 30:70	240	560	Ni/50	1694
ZVI/pum 30:70	240	560	Zn/50	2088
ZVI/pum 30:70	240	560	Cu/500–Ni/50–Zn/50	2088
ZVI/pum 30:70	240	560	Cu/50–Ni/50–Zn/50	2064
ZVI	240	-	Cu/500	1404*
ZVI	240	-	Ni/50	1694
ZVI	240	-	Zn/50	2016*
ZVI	240	-	Cu/500–Ni/50–Zn/50	600*
ZVI	240	-	Cu/50–Ni/50–Zn/50	432*

*test forcedly stopped because of column clogging

8.4 Single-Metal Solutions

8.4.1 Copper

As discussed in §7.4.2, in the column tests carried out using the mixture ZVI/Pumice and the ZVI alone with a contaminant solution of copper at concentration of 500 mg/l pumped with a flow rate of 0.5 ml/min, the contaminant was always removed from solution. Figure 8-1 shows the relative copper concentration versus time calculated at the outlet of the two column systems. The advantage of using a mixture ZVI/Pumice respect to the only ZVI is the ability of the mixture to maintain for a period longer than ZVI a constant permeability (§7.4.3) and to reduce the mass of ZVI to be used with economic advantage.

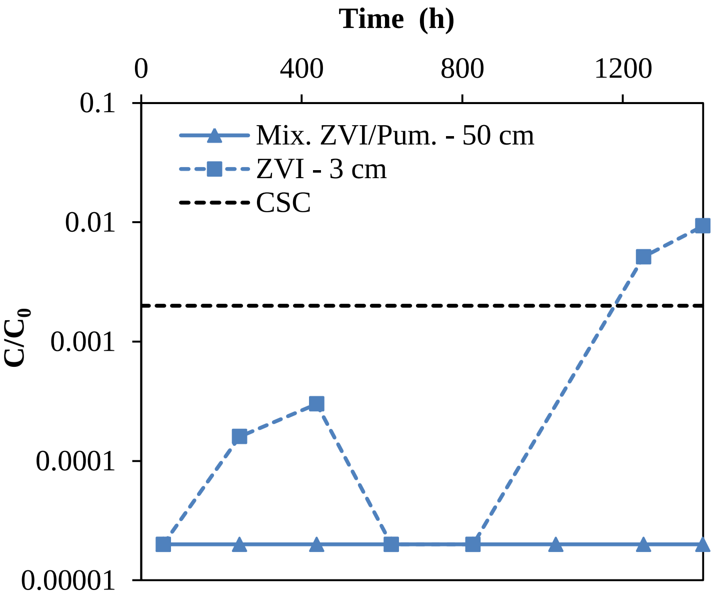


Figure 8-1 Relative copper concentration versus time for the mixture ZVI/Pum. and ZVI

8.4.2 Nickel

Nickel is a contaminant particularly difficult to remove, especially when it is present at high concentration, as previously observed. Figure 8-2 represents Ni breakthrough curves at different sampling ports versus time for the mixture ZVI/Pumice. In the figure the normalized concentration (C/C_0), where C is the effluent concentration and C_0 is the average influent concentration (50 mg/l) over the entire experimental duration, is plotted against time.

It can be observed that Ni concentration reaches the lowest value (< 0.1mg/l) only in the sample withdrawn from the outlet of the column (50 cm) in the first sampling occurred after 55 h from test beginning.

The ZVI used alone shows a removal efficiency lower than the mixture, in fact it is not able to effectively remove the metal, as previously mentioned this fact is due to the shorter residence time that 240 gr of ZVI, which are equivalent to 3 cm of column length, are able to guarantee respect to the mixture using an equivalent amount of iron (Figure 8-3).

For both reactive media the permeability is maintained constant with a slightly decrease (less than 1 order of magnitude) for the ZVI.

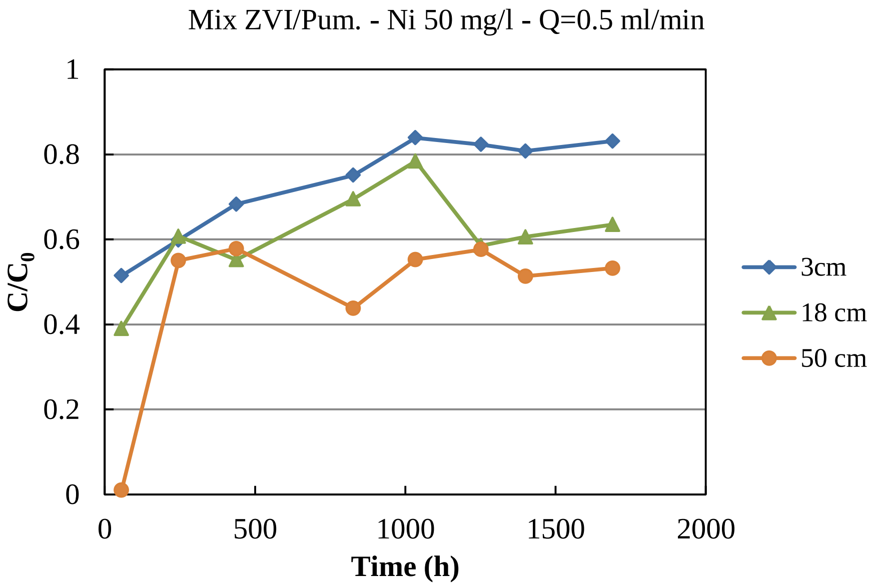


Figure 8-2 Ni breakthrough curve at different sampling ports versus time in the mixture ZVI/Pum. (C_0=50mg/l)

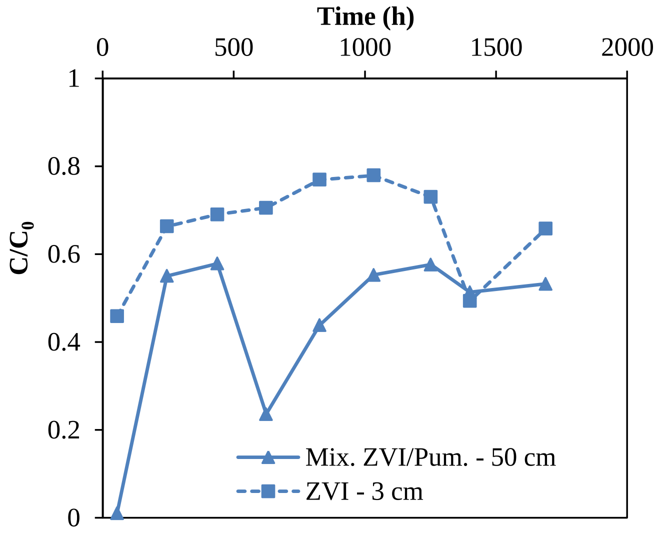


Figure 8-3 Relative nickel concentration versus time for the mixture ZVI/Pum. and ZVI

8.4.3 Zinc

Figure 8-4 represents Zn breakthrough curves at different sampling ports versus time in the mixture ZVI/Pumice. In the figure the normalized concentration (C/C_0), where C is the effluent concentration and C_0 is the average influent concentration (50 mg/l) over the entire experimental duration, is plotted against time. Zinc removal occurs earlier than Nickel removal, in fact its concentration reaches a value lower than limit concentration (3 mg/l) allowed in groundwater by Italian Regulation (D. Lgs. 152/2006) after 18 cm of column length in the first sampling occurred after 55 h from test beginning.

Figure 8-5 shows the relative concentration versus time calculated at the outlet of the column systems containing the mixture ZVI/pumice and the ZVI. Zinc is removed by pure ZVI for a period longer than the mixture (Figure 8-5) but the test was interrupted earlier because of permeability reduction.

As can be observed in Figure 8-6, where the hydraulic conductivity, calculated during column operation for both reactive media, is plotted against time, using ZVI the permeability decreases of 4 order of magnitude after 1000 h of test. Therefore the good compromise between permeability and contaminant removal is guaranteed only by the mixture ZVI/Pumice. By a comparison between nickel and zinc, it can be stated that zinc requires a lower residence time than nickel to be removed from solution. The better removal of Zn respect to Ni is attributable to higher sorption affinity that iron oxides have for Zn than for Ni (Cornell and Schwertmann, 1996; Stumm and Morgan, 1996).

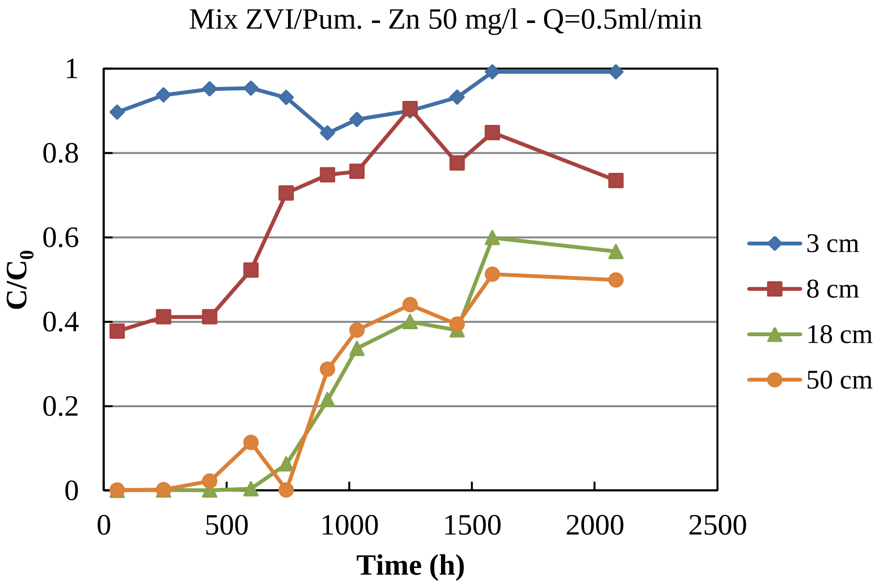


Figure 8-4 Zn breakthrough curve at different sampling ports versus time in the mixture ZVI/Pum. (C_0=50mg/l)

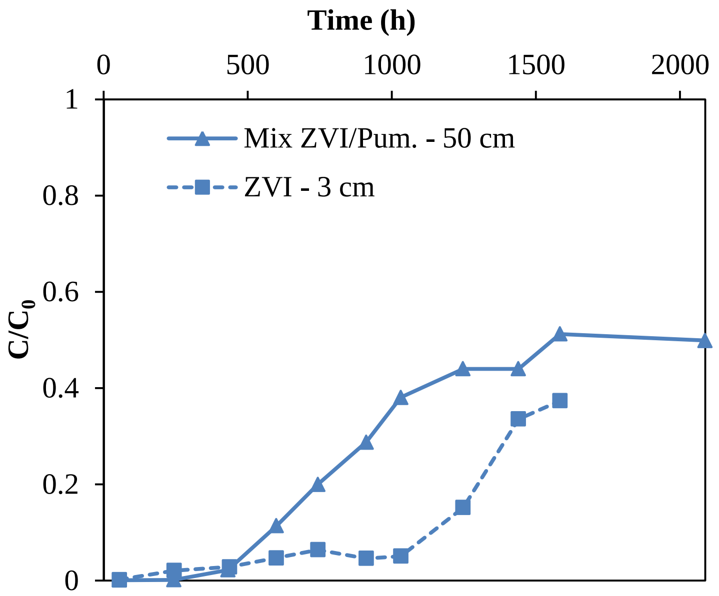


Figure 8-5 Relative Zinc concentration versus time for the mixture ZVI/Pum. and ZVI

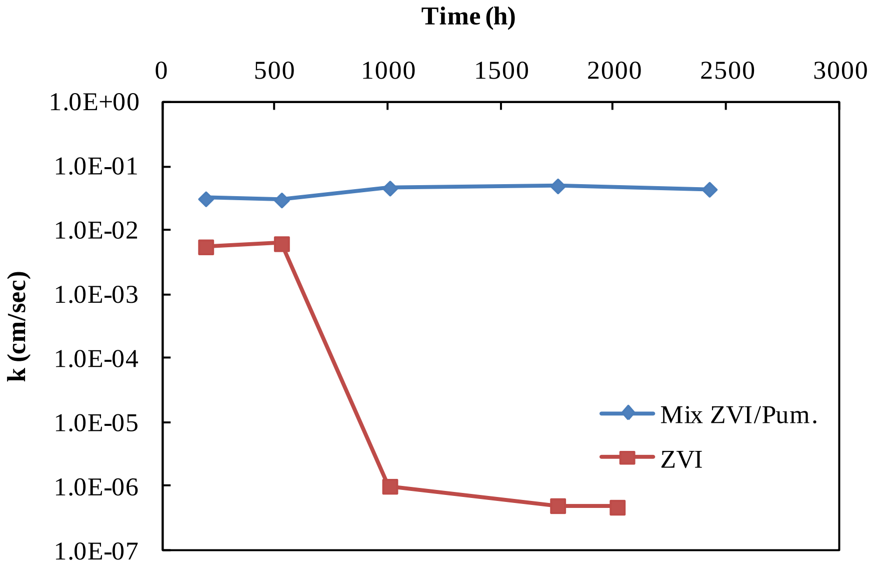


Figure 8-6 Permeability profiles for the mixture ZVI/Pumice and the ZVI with Zn solution

8.4.4 Removal sequence

Results of column tests carried out using single-metal solutions of Cu, Ni and Zn show the following removal sequence Cu > Zn > Ni for either pure ZVI or the mixture ZVI/pumice.

8.5 Three-contaminants solutions

In Figure 8-7, Figure 8-8 and Figure 8-9 are shown the breakthrough curves of the column tests carried out with the granular mixture ZVI/Pumice and the three-contaminants solution (Cu 500 mg/l – Ni 50 mg/l – Zn 50 mg/l) at sampling ports located respectively at 3 cm, 28 cm and 50 cm from inlet.

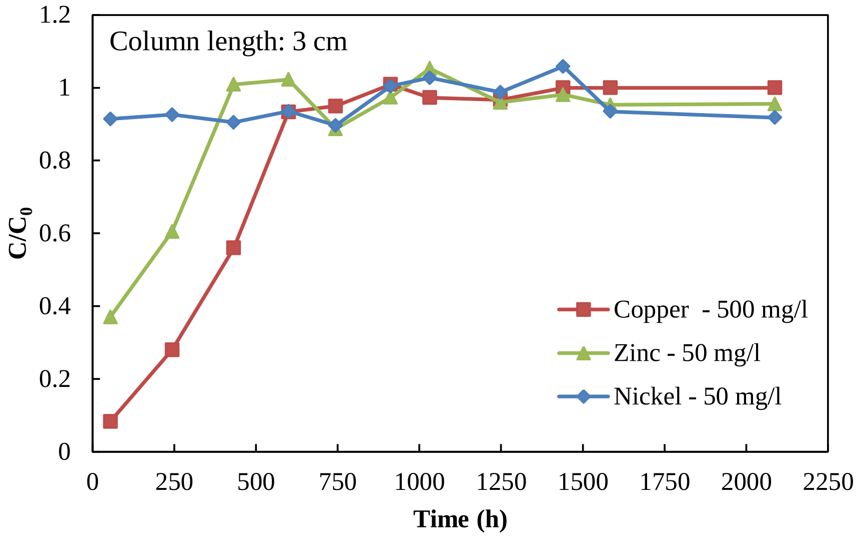


Figure 8-7 Cu, Ni and Zn breakthrough curve at sampling port of 3 cm versus time

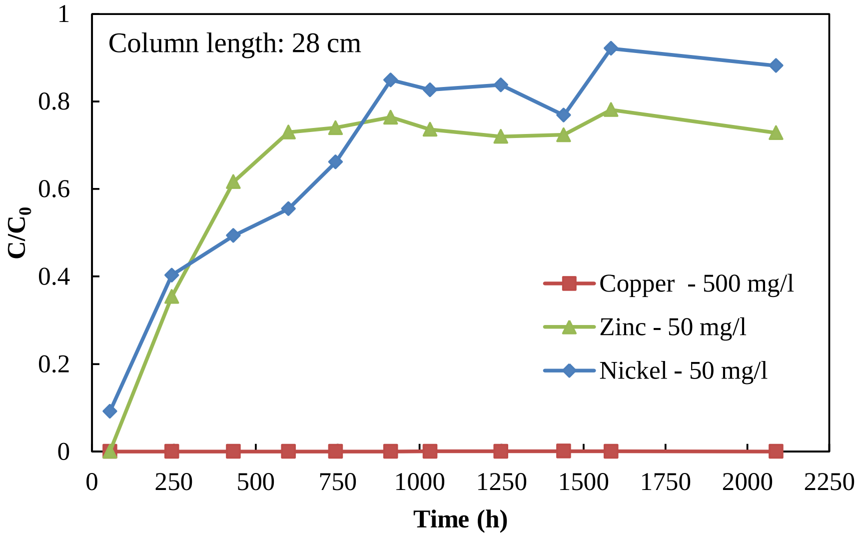


Figure 8-8 Cu, Ni and Zn breakthrough curve at sampling port of 28 cm versus time

Exhaustion of reactive medium toward copper can be observed only in the first sampling port (3 cm of column length) (Figure 8-7), instead at 28 cm and 50 cm of column length the metal concentration is below the concentration limit (1 mg/l) allowed by Italian Regulation. As observed previously (using single-metal-solution) nickel needs a longer residence time to be removed from solution (at least 50 cm of column length) (Figure 8-9).

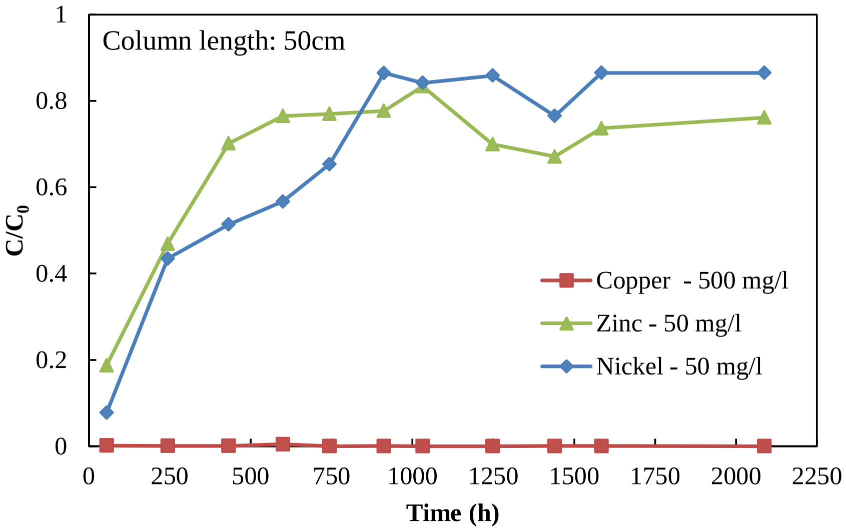


Figure 8-9 Cu, Ni and Zn breakthrough curve at sampling port of 50 cm versus time

Considering 3 cm of column length (Figure 8-7), heavy metals removal follows the same sequence observed for the single-metal-solution (Cu>Zn>Ni) but at 50 cm of column length (Figure 8-9) the removal sequence changes and the removal is higher for Ni than for Zn (Cu>Ni>Zn).

The breakthrough curves for the three contaminants when the reactive medium tested was ZVI are showed in Figure 8-10. Using the ZVI, the duration of the test was lower than the duration of column test with the mixture ZVI/Pumice due to column clogging. Unlike the mixture ZVI/Pumice, when ZVI only is used, the following removal sequence Cu>Zn>Ni is observed. Figure 8-11 shows the relative concentration of the three heavy metals versus time measured at the outlet of the columns of ZVI and the ZVI/Pumice mixture.

Comparing the two reactive media when the same ZVI mass is used, which means a column length of 50 cm for the mixture ZVI/Pumice and 3 cm for the ZVI column, nickel is better removed by the mixture ZVI/Pumice than by the ZVI, on the contrary Zinc is better removed by the ZVI than by the mixture confirming the same behaviour observed when the sing-metal solutions were used.

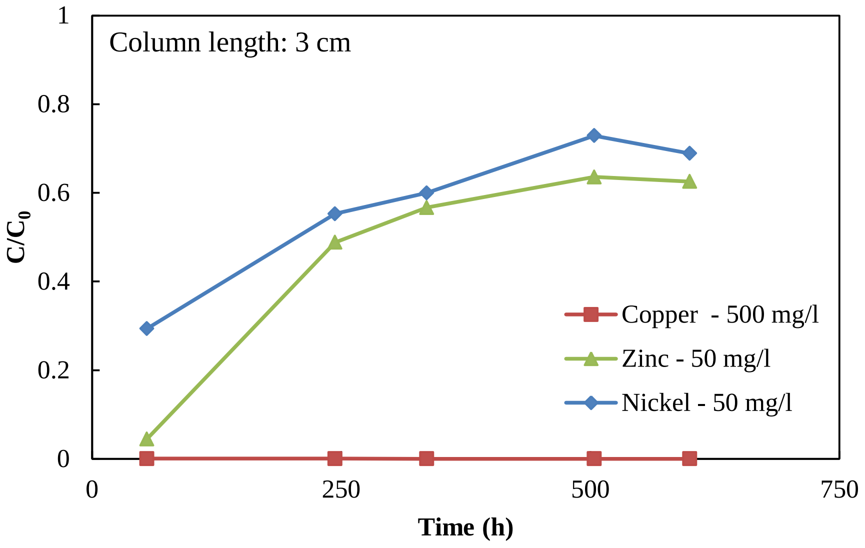


Figure 8-10 Cu, Ni and Zn breakthrough curve at sampling port of 3 cm versus time for the ZVI

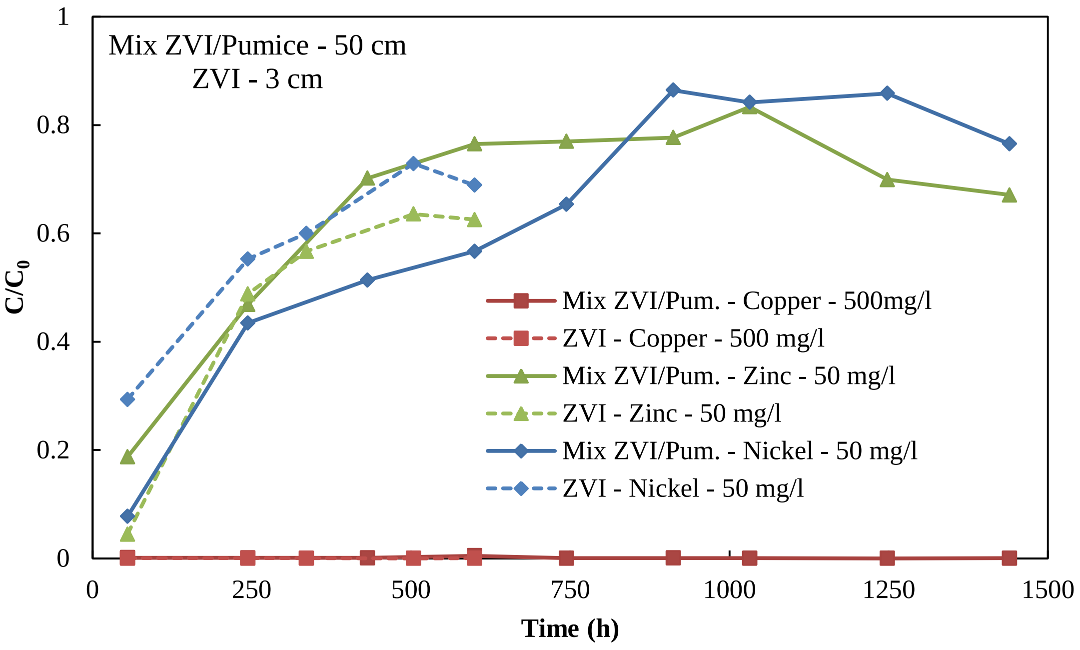


Figure 8-11 Cu, Ni and Zn breakthrough curve versus time for the ZVI and ZVI/pumice mixture

In Figure 8-12, Figure 8-13, and Figure 8-14 are shown the breakthrough curves of the column test with the granular mixture ZVI/Pumice and the three-contaminants solution (Cu 50 mg/l – Ni 50 mg/l – Zn 50 mg/l) at sampling ports located respectively at 3 cm, 28 cm and 50 cm from inlet.

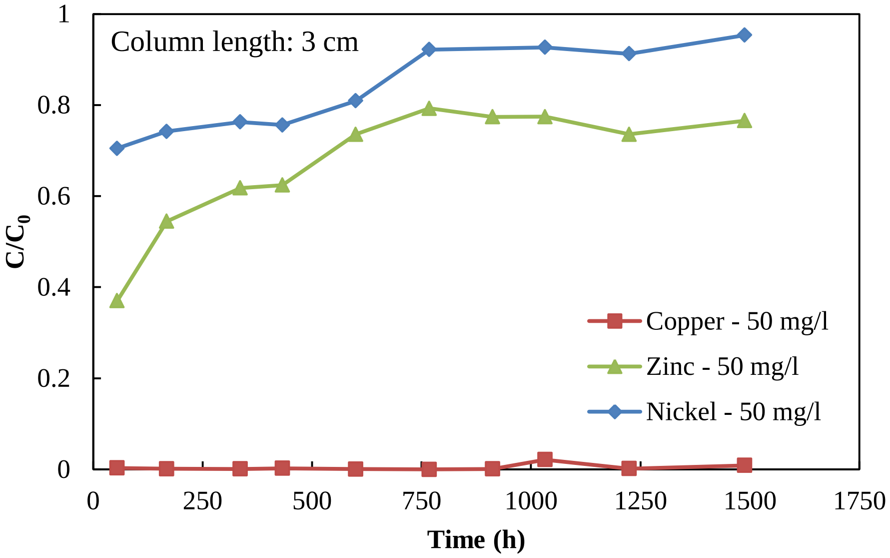


Figure 8-12 Cu, Ni and Zn breakthrough curve at sampling port of 3 cm versus time

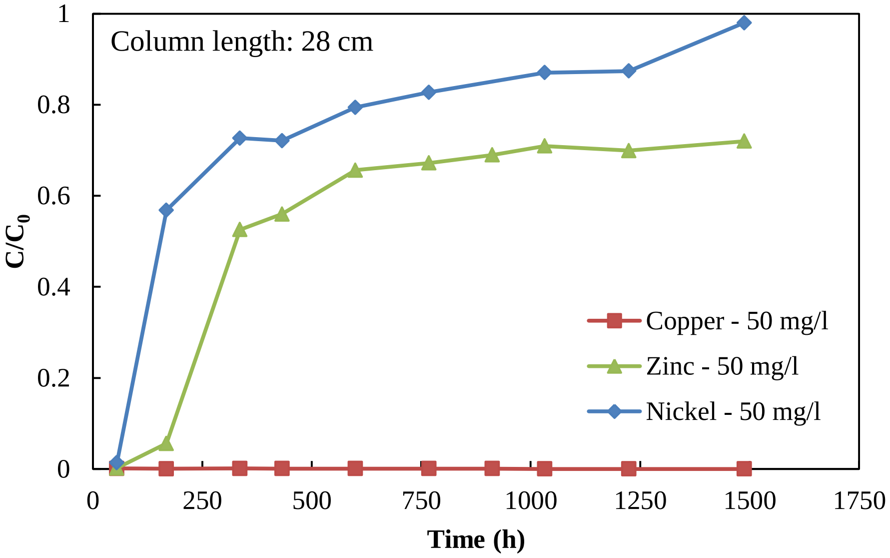


Figure 8-13 Cu, Ni and Zn breakthrough curve at sampling port of 28 cm versus time

Copper is completely removed from solution for all the duration of the test and exhaustion of the medium is not observed. In the first sampling and at 28 cm of column length, Nickel and Zinc are removed from solution (Figure 8-13). The following removal sequence Cu>Zn>Ni is respected during the whole test.

The breakthrough curves for the three metals when the reactive medium tested was the ZVI are showed in Figure 8-15.

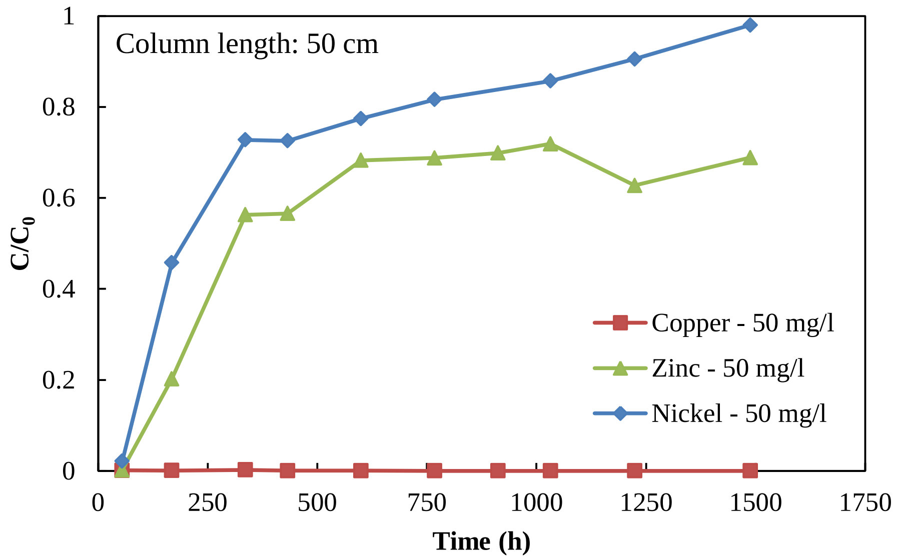


Figure 8-14 Cu, Ni and Zn breakthrough curve at sampling port of 50 cm versus time

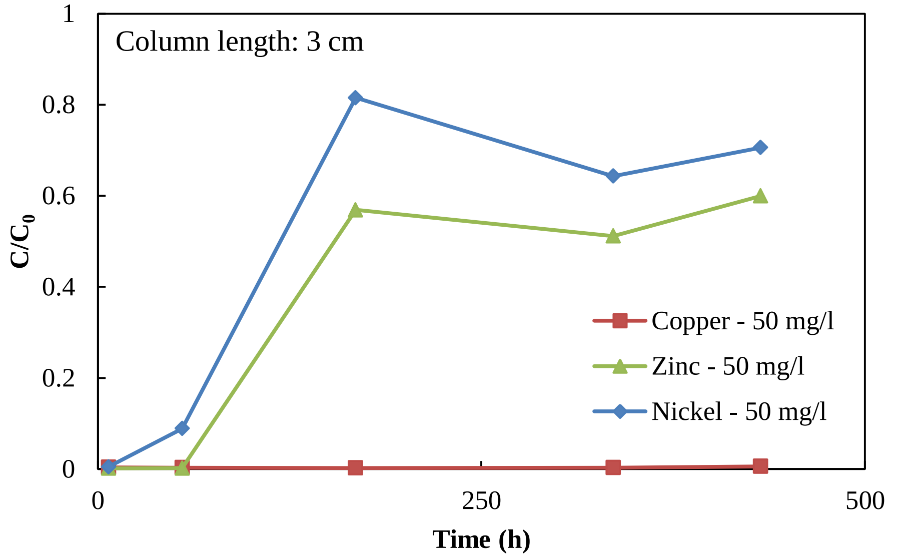


Figure 8-15 Cu, Ni and Zn breakthrough curve at sampling port of 3 cm versus time for the ZVI

Also in this case, the duration of the test was shorter than the column test carried out with the granular mixture due to the clogging of the medium.

Figure 8-16 shows the relative concentration versus time calculated at the outlet of the columns of ZVI and the ZVI/Pumice mixture. Zinc is better removed in the column with the ZVI/Pumice mixture than in the column with ZVI. Nickel is once again better removed by the mixture than by ZVI.

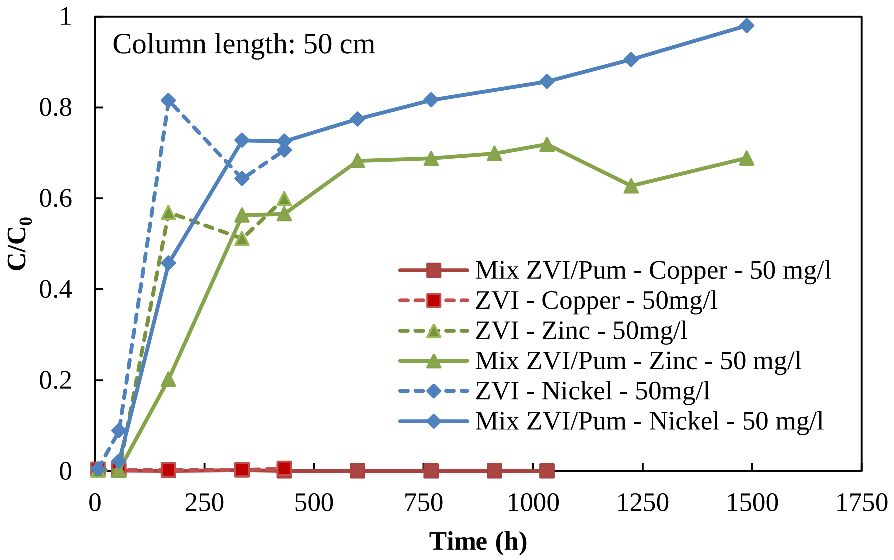


Figure 8-16 Cu, Ni and Zn breakthrough curve versus time for the ZVI and ZVI/pumice mixture

8.6 Single-contaminant and three-contaminants solutions: comparison of performance

Time-dependent evolution of Ni and Zn concentration in the column effluent for single-metal solutions and three-contaminants solutions are summarized in Figure 8-17 and Figure 8-18 respectively. Cu concentration is not reported since its value measured at the outlet rarely exceeds the detection limit of the instrument used (0.1 mg/l) and is always below 0.5 mg/l.

Table 8-2 and Table 8-3 show the removal efficiency, calculated at the outlet of the investigating systems and at different values of contaminant mass in input to the column using equation 23.

In the tests carried out using the three-contaminants solutions and a granular mixture of ZVI and Pumice, copper is unaffected by the presence of the other metals while the removal efficiencies of Ni and Zn decrease respect to mono contaminant tests. It is nevertheless interesting that the removal efficiency reduction is higher for Zn (about 58% respect to the experiment carried out with the solution containing Zn only) than for Ni (reduction of about 33%) leading to very similar removal efficiencies for Ni and Zn but to a change in the sequence that in this case is Cu > Ni > Zn.

Zn removal efficiencies for three-contaminants solutions are considerably reduced respect to the experiments carried out with mono-contaminated solutions.

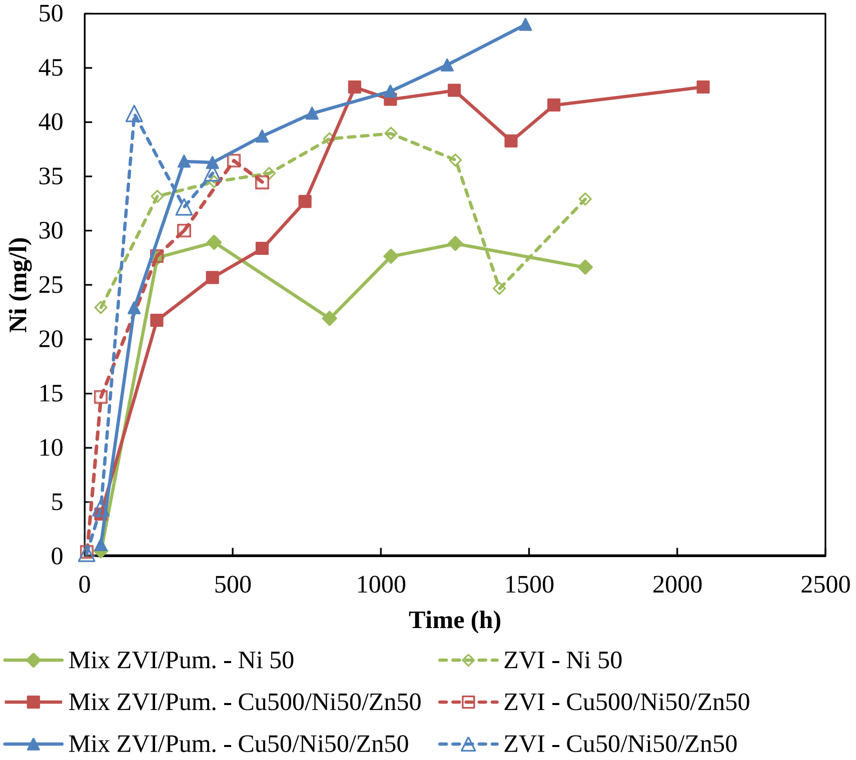


Figure 8-17 Time-dependent evolution of Ni concentration in the column effluent for single-metal solution and three-contaminants solutions

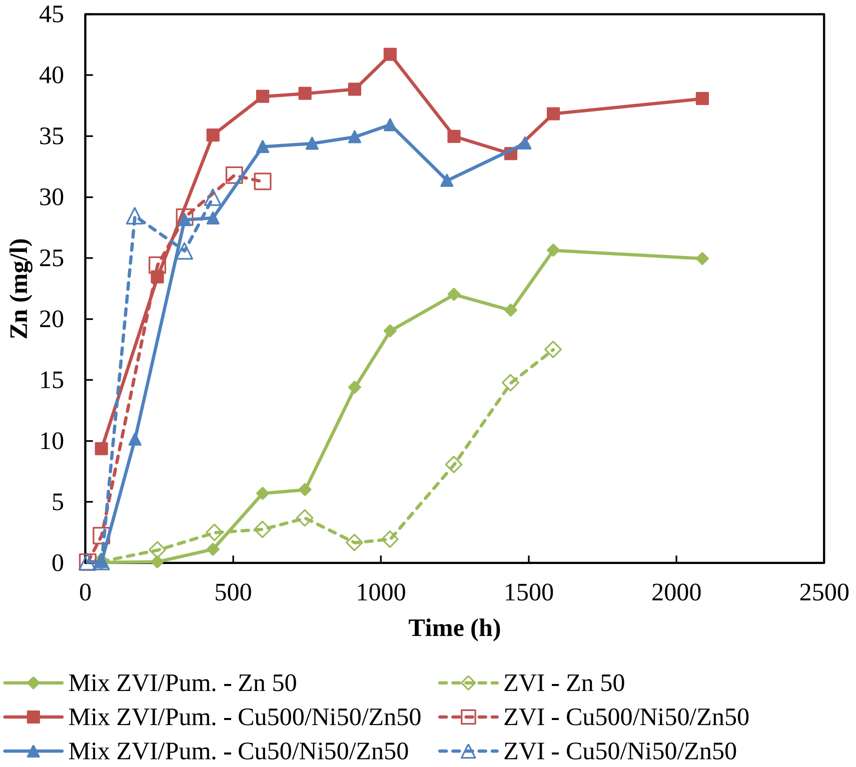


Figure 8-18 Time-dependent evolution of Zn concentration in the column effluent for single-metal solution and three-contaminants solutions

Whereas the comparison of the performance in Ni removal for the column systems where the three-contaminant solutions were used, brings the convincement that most probably copper presence influences positively Ni removal, it is possible that the significant enrichment of the column medium in copper due to the fast cementation of this latter leads to the formation of a bimetallic system between ZVI and Cu that enhances Ni removal. Also if bimetallic systems have been studied in literature (e.g. Hu et al., 2010) data on Ni removal by ZVI/Cu systems are not available.

The fact that in both ZVI systems where the three contaminant solution was used the sequence Cu>Zn>Ni was maintained is attributable to the limited duration of the experiment and to the fact for the already mentioned limited hydraulic residence time Ni removal is less favoured in ZVI systems respect to ZVI/Pumice ones.

Table 8-2: Removal efficiency (E) calculated close the end of the investigated systems

Reactive medium	Contaminant solution	m_i [gr]			E		
		Cu	Ni	Zn	Cu	Ni	Zn
Mix. ZVI/Pum.	Cu 500	21.0	-	-	99,9%	-	-
Mix. ZVI/Pum.	Ni 50	-	2.16	-	-	55.6%	-
Mix. ZVI/Pum.	Zn 50	-	-	2.16	-	-	80.3%
Mix. ZVI/Pum.	Cu500/Ni50/Zn/50	21.0	2.16	2.16	99.7%	37.2%	33.8%
Mix. ZVI/Pum.	Cu50/Ni50/Zn/50	2.23	2.23	2.23	99.9%	25.3%	42.8%
ZVI	Cu 500	21.0	-	-	99.18%	-	-
ZVI	Ni 50	-	2.16	-	-	31.8%	-
ZVI	Zn 50	-	-	2.16	-	-	95.0%
ZVI	Cu500/Ni50/Zn/50	0.9	0.9	0.9	99.8%	46.6%	56.3%
ZVI	Cu50/Ni50/Zn/50	0.65	0.65	0.65	99.8%	44.1%	59.0%

Table 8-3: Removal efficiency (E) calculated at equal contaminant mass in input to the column

Reactive medium	Contaminant solution	m_i [gr]			E		
		Cu	Ni	Zn	Cu	Ni	Zn
Mix. ZVI/Pum.	Cu 500	6.5	-	-	99.88%	-	-
Mix. ZVI/Pum.	Ni 50	-	0.65	-	-	60.6%	-
Mix. ZVI/Pum.	Zn 50	-	-	0.65	-	-	98.7%
Mix. ZVI/Pum.	Cu500/Ni50/Zn50	6.5	0.65	0.65	99.6%	64.7%	54.9%
Mix. ZVI/Pum.	Cu50/Ni50/Zn50	0.65	0.65	0.65	99.9%	51.3%	67.5%
ZVI	Cu 500	6.5	-	-	99.88%	-	-
ZVI	Ni 50	-	0.65	-	-	39.9%	-
ZVI	Zn 50	-	-	0.65	-	-	97.8%
ZVI	Cu500/Ni50/Zn50	6.5	0.65	0.65	99.84%	49.5%	65.3%
ZVI	Cu50/Ni50/Zn50	0.65	0.65	0.65	99.85%	44.1%	59.0%

8.7 kinetic constants for single contaminant and three-contaminant solutions

The contaminant concentrations measured in the first sampling (55 h) of the column tests performed using single metal solutions and three-contaminant solutions were interpreted using equation 1. The kinetic constant obtained are shown in Table 8-4 together with the correlation coefficient (R^2).

Table 8-4 kinetic constant for single metal solutions and three-contaminant solutions

Mezzo reattivo	Contaminant/ C_0[mg/l]	Solution type	k[h^{-1}]	R^2
Mixture ZVI/Pum.	Cu/500	Single metal	5,192	0,78
Mixture ZVI/Pum.	Ni/50	Single metal	0,393	0,92
Mixture ZVI/Pum.	Zn/50	Single metal	1,302	0,87
Mixture ZVI/Pum.	Cu/500	Three-contaminants	1.969	0.76
	Ni/50		0.322	0.89
	Zn/50		0.734	0.82
Mixture ZVI/Pum.	Cu/50	Three-contaminants	3.154	0.54
	Ni/50		0.352	0.76
	Zn/50		1.113	0.97

The highest value of kinetic constant are obtained for copper in single metal solution. The kinetic constant decreases with the following order: Cu>Zn>Ni for single metal and three-contaminants solutions. The kinetic constant of each metal decreases from single metal to three-contaminant solutions. The kinetic constant obtained for nickel are almost similar in the three solutions tested, whereas for zinc and, especially for copper, they change from single metal solution to three-contaminants solution.

8.8 Hydraulic performance

Figure 8-19 shows hydraulic conductivity profile along time for the all column tests performed using single metal and three-contaminants solutions. Excepted for test where a solution containing nickel only was used, all the experiments carried out on column systems containing ZVI only were forcedly interrupted because of tygon tubes disconnection due to the excessive pressure caused by the clogging of the reactive medium. Figure 8-19 clearly shows how the granular mixture between ZVI and Pumice is by far more effective than ZVI alone in maintaining unvaried the hydraulic conductivity in the long term.

Comparing the ZVI column tests using single metal solutions, the faster hydraulic conductivity reduction along time is observed for copper which is the contaminant more easily removed from solution.

Comparing the ZVI column tests using the three-contaminants solutions, the faster hydraulic conductivity reduction is observed when the lowest concentration of copper is used. Between the two solutions used the removal efficiency of the single contaminants is almost similar and slightly better when the highest value of copper concentration is used. Therefore the different hydraulic behaviour between the two column tests is probably linked to the different heavy metal removal mechanisms and to the possible interaction mechanisms among metals.

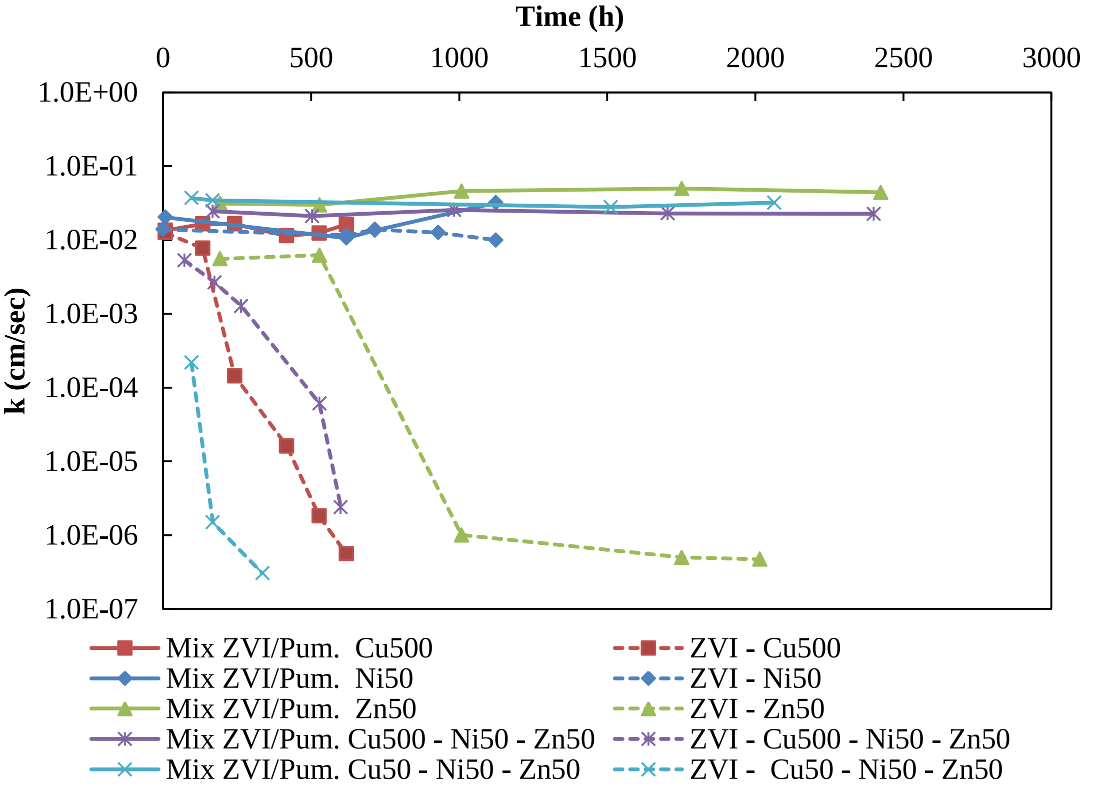


Figure 8-19 Hydraulic conductivity vs. time for single metal and three-contaminants solutions

8.9 Conclusions

Single contaminant solutions of copper, nickel and zinc allowed to investigate the influence of the single heavy metal on the performance of the reactive media composed by ZVI and by the mixture ZVI/Pumice. The following conclusions can be stated:

- ZVI and the granular mixture ZVI/pumice, at w.r. 30:70, are able to remove the heavy metals tested with the following removal sequence: Cu>Zn>Ni.

- Copper is always removed from solutions by the two media. The advantage to use a mixture ZVI/pumice respect to ZVI comes from the lower amount of ZVI required for the barrier design, and from the capacity of the media to maintain a constant value of hydraulic conductivity.

- Considering the same amount of ZVI, Nickel is better removed by the mixture ZVI/Pumice thanks to the higher residence time guaranteed by the presence of pumice.

- Zinc is removed in a similar way by the two media, but also if ZVI in the long time shows higher removal efficiency than the mixture ZVI/pumice, it is not able to maintain the hydraulic conductivity.

The behaviour of both ZVI and the mixture ZVI/Pumice was tested towards three-contaminants solutions of copper, nickel and zinc. The results obtained were compared with column tests performed using single metal solutions at equal metal concentration and using the same amount of reactive medium, which means to consider the same barrier thickness. The following conclusions can be stated:

- the removal efficiency of each metal decreases from single metal solutions to three-contaminant solutions;
- Among the three contaminants, zinc is the heavy metal most sensitive to the presence of the other two contaminants;
- The removal sequence for the mixture ZVI/Pumice using the solution containing 500 mg/l Cu 50 mg/l Ni 50 mg/l Zn changes according to the following sequence Cu>Ni>Zn, therefore contaminants seem to be removed not by individual reactions but during a complex processes of interaction with other contaminants.
- The better removal of nickel in a three-contaminant solution can be due to the enrichment of the column medium in copper. In fact, the fast cementation of this latter leads to the formation of a bimetallic system between ZVI and Cu that can enhance Ni removal.

.

9. CONCLUSIONS AND FUTURE WORK

A PRB is a promising groundwater remediation technology. It consists of a permeable wall filled with a reactive medium and installed perpendicularly to groundwater flow. When contaminated groundwater flows through the barrier, under its natural hydraulic gradient, the reactive medium degrades or trap the contaminants within, through physical, chemical and/or biological processes.

Despite numerous installation of PRBs their long-term performance is not well known. The lifespan of the PRB (duration of time when the barrier is able to intercept the contaminated groundwater and trap the contaminants within), is mainly controlled by reactivity and permeability reduction. In particular, PRB clogging may result in preferential flow, through more permeable zone, or blockage of flow.

Among the possible PRB reactive media, zero valent iron, is the most used, thanks to its ability to treat, with a high removal efficiency, contaminants of different nature, organic and inorganic.

Despite the high removal efficiency of ZVI, the main concern, is the porosity reduction of the iron wall over time. In fact ZVI oxidation and the consequent formation of corrosion products, gases and mineral precipitates are often the cause of the reduction of barrier's permeability.

In particular, iron corrosion products contribute to porosity reduction especially because of their expansive nature, being their volume higher than that of the original metal.

Therefore the selection of the reactive medium for an efficient performance of a PRB, especially in the long term, is actively pursued by the researchers in this field.

In order to avoid the possible clogging of the reactive medium in some application ZVI was mixed with an inert material (e.g. sand).

In this thesis an innovative reactive medium having the objective to prevent permeability loss and also to optimize the use of ZVI, that is quite expensive, is constituted by a granular mixture of ZVI and Pumice proposed in the first time in Moraci et al. (2008).

The reactivity of the innovative medium was experimentally tested for inorganic contaminants (i.e. copper, nickel and zinc) using batch and column tests.

Batch tests allow the selection of the appropriate reactive medium among a wide range of candidate materials.

The objective of batch tests, carried out in this research, was to study the reactivity of ZVI/Pumice granular mixtures in different weight ratio (10:90, 30:70, 50:50, 100:0) in the simultaneous presence of nickel and copper at two different concentrations (5 - 50 mg/l for nickel and 50 – 500 mg/l for copper). Batch tests using mono-contaminated solutions were also carried out and used as benchmark.

The batch experiments show that the ZVI/Pumice mixtures in different weigh ratios are highly effective in removing the two contaminants. When the two contaminants are simultaneously present in the solution, ZVI and the granular mixtures of ZVI/Pumice reveal a selective behaviour toward the two heavy metals: Copper is, in fact, more easily removed from solution and reactions involving Nickel usually begin after complete Copper removal.

Column tests are much more expensive and time-consuming than batch experiments. Column tests provide important information about the behaviour of PRB materials in conditions that more closely approximate those in a reactive barrier system. Column tests represent, at present, the only tool used to determine the design parameters of a PRB.

The column tests were carried out using either pure ZVI or a ZVI/pumice granular mixture with a 30:70 weight ratio. The contaminant solutions tested were single metal and three-contaminants solutions of copper, nickel and zinc.

During column tests, hydraulic conductivity was routinely calculated.

Using single metal solutions the following aspects were studied:

- The effect of initial nickel concentration;
- The effect of flow rate;
- The effect of the acceleration of column tests by means of higher flow rate or higher contaminant concentration respect to in situ conditions.

Nickel concentration influences the behaviour of both reactive media tested in term of removal efficiency and hydraulic performance. In particular, the highest removal efficiency was registered when the lowest initial nickel concentration (i.e. 8 mg/l) was used, whereas using higher contaminant concentration of Ni (i.e. 40 mg/l and 95 mg/l) the removal efficiency of both media was almost similar and slightly better for the highest concentration tested. In term of permeability, in both reactive media tested, a higher permeability decline was observed when the lowest value of Ni concentration was used.

Flow rate also influences the removal efficiency and hydraulic performance of the medium when a solution contaminated by nickel is used. In particular, the best performance in term of removal capacity was registered by the column tests carried out with the lowest flow rate. This behaviour can be easily explained by the longer residence time. The greatest loss of permeability too was observed for the column tests carried out using the lowest value of flow rate. In condition of low flow rate, the precipitation is probably more favoured while using higher flow rates a possible dragging of corrosion products from the pores of the column can be considered.

A comparison between the mixture ZVI/Pumice and ZVI, when the same amount of ZVI is used, has demonstrated the best performance of the mixture in term of removal efficiency and hydraulic performance. Using the ZVI/pumice mixture is beneficial, since increases residence time, enhances the sorption process and promotes contaminant removal. In fact if the two reactive media tested are compared in term of specific removal efficiency (SRC_{ZVI}) (i.e. mass of contaminant removed respect to ZVI mass) the higher values of this index registered for the mixture demonstrate the positive effect of the pumice in maintaining and improving the typical removal capacity of ZVI.

Comparing the behaviour of the two reactive media tested in term of permeability, the mixture showed its capacity to maintain for a period longer than ZVI the permeability.

During some of the column tests, the possible release of Fe at the outlet of columns, derived from iron corrosion, was measured. It was observed an increase of iron concentration that can exceed limit value given by Italian Regulation (i.e. 0.2 mg/l) when the reactive medium started to lose its reactivity.

It can be stated that, a column test accelerated increasing the flow rate or the contaminant concentration underestimates removal efficiency which can be considered a safe procedure in term of PRB design but it is not able to represent the real permeability loss of the medium.

Evaluating the behaviour of the reactive medium in terms of both removal efficiency and permeability is necessary for successful barrier design. Therefore the behaviour of the reactive medium in the long term may be predicted only through column tests carried out under conditions simulating those in situ as closely as possible.

In order to investigate the mineral species generated during the contact of the contaminant solution with the reactive material, at the end of some column tests, the exhausted reactive medium was withdrawn from column and analysed by SEM and XPS.

XPS analyses carried out on the reactive medium composed of pure ZVI, previously in contact with a solution contaminated by nickel, revealed the presence of Ni_2O_3 and NiOH in the first part of the column and the ubiquitous presence of FeOOH, Fe_2O_3 and Fe_3O_4. The presence of needle-like/acicular shape revealed by SEM images seem to confirm the presence of Goethite.

The column tests were also performed using individual and combined solutions of Nickel, Copper and Zinc in order to study phenomena of mutual interaction and/or competition among contaminants.

In the column tests carried out using single-metal solutions and either the pure ZVI or the granular mixture ZVI/pumice, at w.r. 30:70, removal sequence was Cu>Zn>Ni.

Using a three contaminant solution of Cu 500 mg/l, Ni 50 mg/l and Zn 50 mg/l the removal sequence observed for the mixture ZVI/Pumice changes according to the following sequence Cu>Ni>Zn. Among the three contaminants, zinc is the heavy metal most sensitive to the presence of the other two. The better removal of nickel in a three-contaminant solution can be due to the enrichment of the column medium in copper. In fact the fast cementation of this latter probably leads to the formation of a bimetallic system between ZVI and Cu, known in literature as possible reactive medium, that can enhance Ni removal.

Therefore, in a complex system with several contaminants, the removal is probably due not by individual reactions but during a complex processes of interaction with other contaminants.

The experimental activity carried out in this thesis allowed to demonstrate the suitability of a reactive medium constituted by a granular mixture of ZVI and Pumice to be used in a PRB. The ability of this innovative reactive medium to optimizes the use of the pure ZVI, especially in maintaining permeability for a longer time, was also shown. In addiction column tests carried out at various flow rates and initial contaminant concentrations have allowed to evaluate the reliability of column tests to determine the design parameters of a PRB. In particular the behaviour of the reactive medium in the long term may be predicted only through column tests carried out under conditions simulating field conditions as closely as possible. For this reason, it is suggested to carry out in the future column tests operating not only at the same discharge velocity of the contaminated site but also using the groundwater derived from the same site. In fact constituents such as calcium and carbonate present in the contaminated site could influence the performance of the reactive medium in term of both removal efficiency and hydraulic conductivity. For a better evaluation of the suitability of the innovative material, pilot experiments in situ would be also beneficial.

Some current researches are also focusing their attention on the possible causes of medium porosity reduction over time through numerical simulation of porosity evolution observed in ZVI systems. Efforts have to be done in particular to develop a model able to take in account all possible causes of porosity reduction: the expansive nature of iron corrosion products, gas production and precipitates generated by constituents present in the water and by the reaction among the compounds, the contaminants and the reactive medium.

References

- Ambrosini G. S. D., 2004. *Reactive Materials for Subsurface Remediation through Permeable Reactive Barriers*. A dissertation submitted for the degree of doctor of sciences to the Swiss federal institute of technology Zurich.

- Amin H., 2008. *Design methodology for permeable reactive barriers combined with monitored natural attenuation*. Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University In partial fulfillment of the requirements for the degree of Master of Science.

- Baciocchi R., Boni M.R., D'Aprile L., 2003. *Characterization and Performance of Granular Iron as Reactive Media for TCE degradation by Permeable Reactive Barriers*. Water air soil pollution, 149 (1-4), pp. 211-226.

- Badruzzaman M., and Westerhoff P., 2005. *The Application of Rapid Small-Scale Column Tests in Iron-Based Packed Bed Arsenic Treatment Systems*. Advances in arsenic research: integration of experimental and observational studies and implications for mitigation, American Society of Chemistry, New York, pp. 268–283.

- Bang S., Johnson M.D., Korfiatis G.P., Meng X., 2005. *Chemical reactions between arsenic and zero-valent iron in water*. Water Research, 39, pp. 763–770.

- Bartzas G., Komnitsas K., Paspaliaris I., 2006. *Laboratory evaluation of* Fe^0 *barriers to treat acidic leachates. Minerals Engineering* , 19, pp. 505–514.

- Bear J., 1972. *Dynamics of Fluids in Porous Media*. American Elsevier, New York.

- Benner S.G., Gould W.D., Blowes D.W., 2000. *Microbial populations associated with the generation and treatment of acid mine drainage*. Chemical Geology, 169, pp. 435–448.

- Blowes D.W. and Ptacek C. J., 1992. *Geochemical remediation of groundwater by permeable reactive walls: Removal of chromate by reaction with iron-bearing solids*. Proc., Subsurface Restoration Conference, Dallas, TX, pp. 214-216.

- Blowes D.W., Ptacek C.J. and Jambor J.L. , 1997. *In-situ Remediation of Cr(VI) Contaminated Groundwater using Permeable Reactive Walls: Laboratory Studies*. Environmental Science and Technology, 31(12), pp. 3348-3357.

- Blowes D.W., Ptacek C.J., Benner S.G., Waybrant K.R., Bain J.G., 1998. *Porous reactive walls for the prevention of acid mine drainage: a review.* Min. Proc. Ext. Met. Rev., 19, pp.25–37.

- Blowes D.W., Puls R.W., Gillham R.W., Ptacek C.J., Bennet, T., Bain J.G., Hanton-Fong C.J., and Paul C.J., 1999. *An In-Situ Permeable Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Ground Water: Volume 2 Performance Monitoring.* United States Environmental Protection Agency, Cincinnati, OH, Report EPA/600/R-99/095b.

- Blowes D.W., Ptacek C.J., Benner S.G., McRae C.W.T., Bennet T.A., Puls R.W., 2000. *Treatment of inorganic contaminants using permeable reactive barrier. Journal of Contaminant Hydrology*, 45, pp. 123-137.

- Bonin P. M. L., Odziemkowski E. J., Reardon E. J., Gillham R., 2000. *W. J. Sol. Chem.*, 29, pp. 1061-1074.

- Bronstein K, 2005. *Permeable Reactive Barriers for Inorganic and Radionuclide Contamination*, http://www.clu-in.org.

- Calabrò P.S., Moraci N., Suraci P., 2011. *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.* Journal of Hazardous Materials doi:10.1016/j.jhazmat.2011.06.094.

- Cantrell K.J., Kaplan D.I., Wietsma T.W., 1995. *Zero-valent iron for the in situ remediation of selected metals in groundwater*. Journal of Hazardous Materials, 42, pp. 201-212.

- Caré S., Nguyen Q.T., L'Hostis V., Berthaud Y., 2008. *Mechanical properties of the rust layer induced by impressed current method in reinforced mortar.* Cement Concrete Res., 38 (8-9), pp. 1079–1091.

- Chapuis R. P., and M. Aubertin. 2003. *On the use of the Kozeny-Carman equation to predict the hydraulic conductivity of soils.* Canadian Geotechnical Journal, 40 (3), pp. 616-628.

- Charbeneau R. J., 2000. *Advection-Dispersion Transport and Models*, in Groundwater Hydraulics and Pollutant Transport, edit by M. Horton, E. Clark, and V. O'Brien, Prentice-Hall, Inc., Upper Saddle River, NJ 07458, pp 365-457.

- Chun Kit L., 2000. *Laboratory and full-scale studies of a permeable reactive barrier on the dechlorination of chlorinated aliphatic hydrocarbons.* Ph.D. Thesis, Hong Kong University of Science and Technology.

- Cornell R.M., and Schwertmann U., 1996. *The Iron oxides.* VCH, Verlagsgesellschaft, Weinheim, pp. 573.

- Courcelles B., Farahmand-Razavi A.M., Gouvenot D., Esnault-Filet A., 2008a. *Testing and Modeling the Hydraulic Permeability Evolution of Permeable Reactive Barriers Clogged by Colloids.* The 12th International Conference of International Association for Computer Methods and Advances in Geomechanics (IACMAG) 1-6 October, 2008 Goa, India.

- Courcelles B., Farahmand-Razavi A.M., Gouvenot D., Esnault-Filet A., 2008b. *Predictive Model to Design the Permeable Reactive Barrier filters.* The 12th International Conference of International Association for Computer Methods and Advances in Geomechanics (IACMAG) 1-6 October, 2008 Goa, India.

- Crawford R. J., Harding I. H., and Mainwaring D. E., 1993. *Adsorption and coprecipitation of single heavy metal ions onto the hydrated oxides of iron and chromium.* Langmuir, 9, pp. 3035–3056.

- Crittenden J. C., Reddy P. S., Arora H., and Hand J. T. D. W., 1991. *Predicting GAC performance with Rapid Small-Scale Column Tests.* Journal AWWA, Jan.

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

- Day S.R., O'Hannesin S.F., Marsden L., 1999. *Geotechnical techniques for the costruction of reactive barriers.* Journal of Hazardous Materials, 67 (3), pp. 285-297.

- Di Molfetta A., Sethi R., 2006. *Clamshell excavation of a permeable reactive barrier.* Environmental geology, Springer Berlin/Heidelberg, March.

- Di Molfetta A., Sethi R., 2005. *The first permeable reactive barrier in Italy.* Proceedings of the 9th International FZK/TNO Conference on Soil Water Systems, Bordeaux 3-7 October 2005.

- Diels L., van der Lelie N., Bastiaens L., 2002. *New developments in treatment of heavy metal contaminated soils.* Reviews in Environmental Science and Biotechnology, 1(1), pp.75–82.

- Dries J., Bastiaens L., Springael D., Kuypersc S., 2005. *Effect of humic acids on heavy metal removal by zero-valent iron in batch and continuous flow column systems.* Water Research, 39, (15), pp. 3531–3540.

- Dias R.P., Teixeira J.A., Mota M.G., Yelshin A.I., 2004. *Particulate binary mixtures: dependence of packing porosity on particle size ratio.* Ind. Eng. Chem. Res., 43 (24), pp. 7912–7919.

- Dwyer B. P., 2000. *Evaluation of a Permeable Reactive Barrier Technology for use at Rocky Flats Environmental Technology Site (RFETS).* Albuquerque, NM: Sandia National Laboratories, Report # SAND-2000-0075.

- EPA, 2000. *In situ treatment of soil and groundwater contaminated with chromium.* EPA 625/R-00/004.

- EPA, 2002. *Field Applications of in Situ Remediation Technologies: Permeable Reactive Barriers.* Washington, D.C.: United States Environmental Protection Agency, Office of Solid Waste and Emergency Response.

- Ersoy B., Sariisik A., Dikmen S., Sariisik G., 2010. *Characterization of acidic pumice and determination of its electrokinetic properties in water.* Powder Technology, 197 (1-2), pp.129–135.
- Farrell J., Kason M., Melitas N., and Li T., 2000. *Investigation of the Long-Term Performance of Zero-Valent Iron for Reductive Dechlorination of Trichloroethylene.* Environ. Sci. Technol., 34 (3), pp 514–521.
- Fetter C.W., 1999. *Contaminant Hydrogeology*, 2nd edition, edited by R. A. McConnin, Prentice-Hall, Inc., Simon & Schuster/A Viacom Company, Upper Saddle River, New Jersey 07458, USA.
- Fiore S., Zanetti M.C., 2009. *Preliminary Tests Concerning Zero-Valent Iron Efficiency in Inorganic Pollutants Remediation.* American Journal of Environmental Sciences, 5 (4), pp.555-560.
- Furukawa Y., Kim J., Watkins J., Wilkin R.T., 2002. *Formation of Ferrihydrite and Associated Iron Corrosion Products in Permeable Reactive Barriers of Zero-Valent Iron.* Journal of Environmental Science and Technology, 36 (24), pp. 5469-5475
- Fruchter J. S., 2002. *In situ treatment of chromium-contaminated groundwater.* Environmental Science & Technology, 36 (23), pp. 464-472.
- Gavaskar A. R., Gupta N., Sass B., Fox T., Janosy R. J., Cantrell K., Olfenbuttel R., 1997. *Design guidance for application of Permeable reactive barriers to remediate Dissolved Chlorinated Solvents.* DG1110-345-117.
- Gavaskar A.R., 1999. *Design and costruction techniques for permeable reactive barriers.* Journal of Hazardous Materials, 68 (1-2), pp. 41-77.
- Gavaskar A. R., Gupta N., Sass B., Fox T., Janosy R. J., and Hicks J. T., 2000. *Design guidance for application of permeable reactive barriers for groundwater remediation.* Report Prepared for the US-AIR FORCE, Battelle, Columbus, Ohio.
- Gillham R.W. & O'Hannesin S.F., 1994. *Enhanced degradation of halogenated aliphatics by zero-valent iron.* Ground Water, 32(6), 958-967.
- Gibb J.P., Barcelona M.J., Ritchey J.D., LeFaivre M.H., 1984. *Effective porosity of geologic materials: first annual report.* Champaign, Ill; Illinois State Water Survey. SWS contract report 351 (1984).
- Gu B.,. Watson D. B, Phillips D. H., and Liang. L. Y., 2002. *Biogeochemical, Mineralogical, Hydrological Characteristics of an Iron Reactive Barrier used for Treatment of Uranium and Nitrate.* In Handbook of Groundwater Remediation using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals, and Nutrients, eds. David L. Naftz, Stan J. Morrison, James A. Davis and Christopher C. Fuller, 305-342. San Diego, CA: Academic Press.

- Gupta N., Fox T.C., 1999. *Hydrogeologic modeling for permeable reactive barriers.* Journal of Hazardous Materials, 68 (1-2), pp. 19–39.
- Henderson A.D., 2004. *Solids Formation and Permeability Reduction in Zero-Valent Iron and Iron Sulfide Media for Permeable Reactive Barriers.* Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Environmental Engineering) in The University of Michigan.
- Henderson A.D., Demond A.H., 2007. *Long-Term Performance of Zero-Valent Iron Permeable Reactive Barriers: A Critical Review.* Environmental Engeenering Science, 24 (4), pp. 401-423.
- Henderson A.D., Demond A.H., 2012. *Impact of Solids Formation and Gas Production on the Permeability of ZVI PRBs.* Journal of Environmental Engineering, 137 (8), pp. 689-696.
- Hocking G., Wells S. L., and Ospina R. I., 1998. *Performance of the Iron Reactive Permeable Barrier at Caldwell Superfund Site.* RTDF Meeting, Oak Ridge, TN, November 17-18.
- ITRC (Interstate Technology & Regulatory Council) 2005. *Permeable Reactive Barriers: Lessons Learned / New Directions.* Washington, D.C.: Interstate Technology & Regulatory Council, PRB: Technology Update Team. www.itrcweb.org.
- ITRC (Interstate Technology & Regulatory Council) 2011. *Permeable Reactive Barrier: Technology Update.* PRB-5. Washington, D.C.: Interstate Technology & Regulatory Council, PRB: Technology Update Team. www.itrcweb.org.
- Jeen S. W., Gillham R. W., and Blowes D. W., 2006. *Effects of carbonate precipitates on long-term performance of granular iron for reductive dechlorination of TCE.* Environmental Science & Technology, 40 (20), pp. 6432-6437.
- Jury, W. A., and R. Horton. 2004. *Soil Physics.* 6th ed. Hoboken, N.J.: John Wiley.
- Kamolpornwijit W., Liangb L., West O.R., Moline G.R., Sullivana A.B., 2003. *Preferential flow path development and its influence on long-term PRB performance: column study.* Journal of Contaminant Hydrology, 66 (3-4), pp. 161– 178.
- Kiilerich O., Larsen J. W., Nielsen C., and Deigaard L. D., 2000. *Field results from the use of a permeable reactive wall.* Paper presented at Chemical Oxidation and Reactive Barriers: Remediation of Chlorinated and Recalcitrant Compounds: The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 22-25.
- Komnitsas K., Bartzas G., Paspaliaris I., 2006. *Inorganic contaminant fate assessment in zero-valent iron treatment walls.* Environmental forensics, 7 (3), pp. 207 - 217.
- Komnitsas K., Bartzas G., Fytas K., Paspaliaris I., 2007. *Long- term efficiency and kinetic evaluation of ZVI barriers during clean-up of copper containing solutions.* Minerals engineering, 20 (13), pp. 1200-1209.

- Korte N. E., West O. R., Liang L. Y., Pelfrey M. J., and Houk T. C., 1997. *A field-scale test facility for permeable reactive barriers at the Portsmouth Gaseous Diffusion Plant.* Federal Facilities Environmental Journal, 8 (3), pp. 105-114.

- Lackovic J.A., Nikolaidis N.P., and Dobbs G.M., 2000. *Inorganic Arsenic Removal by Zero-valent Iron.* Environmental Engineer and Science, 17(1), 29-39.

- Le Gallo Y., Bildstein O., Brosse E., 1998. *Coupled reaction-flow modeling of diagenetic changes in reservoir permeability, porosity and mineral compositions*. J. Hydrol. 209, 366–388.

- Li, L., Benson, C.H., Lawson, E.M., 2005. *Impact of mineral fouling on hydraulic behaviour of permeable reactive barriers.* Ground Water 43 (4), 582– 596.

- Li L., Benson C.H., Lawson E.M., 2006. *Modeling porosity reductions caused by mineral fouling in continuos-wall permeable reactive barriers.* Journal of Contaminant Hydrology, 83 (1-2), pp. 89-121.

- Li X., and Zhang W., 2008. *Sequestration of Metal Cations with Zerovalent Iron Nanoparticless. A Study with High Resolution X-ray Photoelectron Spectroscopy (HR-XPS).* J. Phys. Chem. C, 111 (19), pp. 6939-6946.

- Liang L. Y., Korte N. E., Gu B., Puls R., and Reeter C., 2000. *Geochemical and microbial reactions affecting the long-term performance of in situ 'iron barriers'.* Advances in Environmental Research, 4 (4), pp. 273-286.

- Liang, L. Y., Sullivan A. B., West O. R., Moline G. R., and Kamolpornwijit W., 2003. *Predicting the precipitation of mineral phases in permeable reactive barriers.* Environmental Engineering Science, 20 (6), pp. 635-653.

- Mackenzie P.D., Horney D.P., Sivavec T.M., 1999. *Mineral precipitation and porosity losses in granular iron columns.* Journal of Hazardous Materials, 68 (1-2), pp. 1-17.

- Mayer K.U., Blowes D.W., Frind E.O., 2001. *Reactive transport modeling of an in situ reactive barrier for the treatment of hexavalent chromium and trichloroethylene in groundwater.* Water Resources Research, 37 (12), No. 12.

- Melitas N., Farrell J., 2002. *Understanding chromate reaction kinetics with corroding iron media using Tafel analysis and electrochemical impedance spectroscopy.* Environmental Science and Technology, 36 (24), pp. 5476-5482.

- Moraci N., Rigano G., Suraci, P., Calabrò P.S., Panzera G., Antonucci P.L., 2008. *Studio sperimentale sull'efficienza di barriere permeabili reattive per la bonifica di acque di falda contaminate da metalli pesanti.* In Atti del Simposio Internazionale di Ingegneria Sanitaria e Ambientale SIDISA 2008. Firenze - 24 - 27 Giugno 2008. (In Italian).

- Moraci N., and Calabrò P.S., 2010. *Heavy metals removal and hydraulic performance in zero-valent iron/pumice permeable reactive barriers.* J. Environ. Manage., 91(11), pp. 2336-2341.

- Moraci N., Calabrò P. S., Bilardi S., 2010a. *Efficency of Zero valent iron/Pumice granular mixtures in simultaneous removal of copper and Nickel.* Proc. of the Second International Conference Hazardous and Industrial Waste Management, Chania (Creta).

- Moraci N., Calabrò, P. S., Suraci, P., 2010b. *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.* Proc. of the Second International Conference Hazardous and Industrial Waste Management, Chania (Creta).

- Moraci N., Calabrò P. S., Suraci P. 2011. *Long-Term Efficiency of Zero-Valent Iron - Pumice Granular Mixtures for the Removal of Copper or Nickel From Groundwater.* Soils and Rocks, 34(2), pp.129-137.

- Morrison S.J., Metzler D.R., Dwyer B.P., 2002. *Removal of As, MN, Mo, Se, U, V and Zn from groundwater by zero-valent iron in a passive treatment cell: reaction progress modeling.* Journal of Contaminant Hydrology, 56 (1-2), pp. 99-166.

- Morrison S. J., Mushovic P. S., and Niesen P. L., 2006. *Early breakthrough of molybdenum and uranium in a permeable reactive barrier.* Environmental Science and Technology, 40 (6), pp. 2018-2024.

- Mountjoy K.J., Pringle E.K., Choi M., Gowdy W. 2003. *The Use of Permeable Reactive Barriers for In-situ Remediation of Groundwater Contaminants.* ESAA Remediation Technologies Symposium, October 15-17, 2003.

- Noubactep, C., Meinrath, G., Merkel, B.J., 2005. *Investigating the mechanism of uranium removal by zero-valent iron.* Environ Chemistry, 2 (3), 235–242.

- Noubactep C., 2006. *Contaminant reduction at the surface of elemental iron: the end of a myth.* Wiss. Mitt. Institut für Geologie der TU Bergakademie Freiberg, Band 31 — ISSN 1433-1284, pp. 173-179.

- Noubactep C., 2009. *An analysis of the evolution of reactive species in Fe0/H2O systems.* Journal of Hazardous Materials,168 (2-3), pp. 1626–1631.

- Noubactep C., Schöner A., 2009. *Fe^0-based alloys for environmental remediation: Thinking outside the box.* Journal of Hazardous Materials, 165 (1-3), pp. 1210–1214.

- Noubactep C., 2010. Metallic iron for safe drinking water worldwide. Chemical Engineering Journal, Vol. 165 (2), pp. 740-749.

- Nutting P. G. , 1930. *Physical analysis of oil sands.* American Association of Petroleum Geologists Bulletin, 14 (1), pp. 1337-1349.

- O J., Jeen S., Jeen S., Gillham R.W., Giu L., 2009. *Effect of initial corrosion rate on long-term performance of iron reactive barriers: Column experiments and numerical simulation.* Journal of Contaminant Hydrology, Vol. 103 (3-4), pp.145-156.

- O'Hannesin S.F., Gillham R.W., 1998. *Long term performance of an in situ "Iron Wall" for Remediation of VOCs.* Ground Water, 36 (1), pp. 164-170.

- Painter B.D.M., 2005. *Optimisation of Permeable Reactive Barrier Systems for the Remediation of Contaminated Groundwater.* A thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at Lincoln University.

- Phifer M. A., Sappington F. C., Nichols R. L., Ellis W.N., Cardoso-Neto J.E., 1999. *Geosiphon/geoflow treatment systems* .WM'99 conference, february 28 - march 4.

- Phillips D.H., Gu B., Watson D.B., Roh Y., Liang L., and Lee S.Y., 2000. *Performance evaluation of a zerovalent iron reactive barrier: Mineralogical characteristics.* Environ. Sci. Technol., 34(19), pp. 4169–4176.

- Phillips D. H., Watson D. B., Roh Y., Gu B., 2003. *Mineralogical Characteristics and Transformations during Long-Term Operation of a Zerovalent Iron Reactive Barrier.* Journal of Environmental Quality, 32 (6), pp. 2033-2045.

- Ponder S.M., Darab J.G., and Mallouk T.E., 2000. *Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron.* Environ. Sci. Technol., 34 (12), pp. 2564–2569.

- Prasad P. V. V. V., Das C., Golder A. K. , 2011. *Reduction of Cr(VI) to Cr(III) and removal of total chromium from wastewater using scrap iron in the form of zerovalent iron(ZVI): Batch and column studies.* Can. J. Chem. Eng., 89 (6), pp. 1575-1582.

- Puls R.W., Blowes D.W., Gillham R.W., 1999. *Long-term performance monitoring for permeable reactive barrier at the U.S. Coast Guard Support Center, Elisabeth City, North Carolina.* Journal of Hazardous Materials, 68 (1-2), pp. 109-124.

- Pumex spa, Lipari Pumice. Website http://www.pumex.it/pumex%20inglese.pdf. Accessed 01/12/2010.

- Rabideau A. J., Suribhatla R., and Craig J. R., 2005. *Analytical models for the design of iron-based permeable reactive barriers.* J. Environ. Eng., 131 (11), pp. 1589–1597.

- Rangsivek R., Jekel M.R., 2005. *Removal of dissolved metals by zero-valent iron (ZVI): Kinetics, equilibria, processes and implications for stormwater runoff treatment.* Water Resources, 39 (17), pp. 4153-4163.

- Rigano G., 2007. *Studio dell'efficienza di barriere permeabili reattive per la bonifica di acquiferi contaminati da metalli pesanti.* Ph. D. Thesis in Geotechnical Engineering in The Mediterranean University of Reggio Calabria.

- Roberts L. R., Ball W. P., Searson P., Fairbrother H., Vikesland P. J., Klausen J., Zimmermann H. J., and Burris D. R., 2002. *Final Report for the SERDP Project CU-218 1125: Influence of Groundwater Constituents on Longevity of Iron-Based Permeable Barriers.* Baltimore, MD: John Hopkins University, Report # CU-1125.

- Roh Y., Lee S.Y., Elless M.P., 2000. *Characterization of corrosion products in the permeable reactive barriers.* Environmental Geology, 40 (1-2), pp. 184-194.

- RTDF 2002 Permeable Reactive Barrier Installation Profiles <www.rtdf.org/public/permbarr/prbsumms/> Remediation Technologies Development Forum. April.

- Sarr D., 2001. *Zero-valent iron permeable reactive barriers - how long will they last?* Remediation: The Journal of Environmental Cleanup Costs, Technologies & Techniques, 11 (2), pp. 1-18.

- Scherer M. M., Richter S., Valentine R. L., and Alvarez P. J. J., 2000. *Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean up. Critical Reviews.* Environmental Science and Technology, 30 (3), pp. 363-411.

- Schultz D.S., Landis R. C., 1998. *Design and Cost Estimation of Permeable Reactive Barriers.* Remediation winter, 9 (1), pp. 57–67.

- Shokes T.E., Möller G., 1999. *Removal of Dissolved Heavy Metals from Acid Rock Drainage Using Iron Metal.* Environ. Sci. Technol., 33 (2), pp 282–287.

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

- Smith J.W.N., Boshoff G. and Bone B.D., 2003. *Good practice guidance on permeable reactive barriers for remediating polluted groundwater, and a review of their use in the UK Land.* Contamination & Reclamation, 11 (4), pp. 411-418.

- Sridharan N. and Lee G. F., 1972. *Coprecipitation of Organic Compounds from Lake Water by Iron Salts.* Environ. Sci. & Technol., 6 (12), pp.1031-1033.

- Steefel C.I. , and Lasaga A.C. , 1990. *The evolution of dissolution patterns: Permeability change due to coupled flow and reaction.* In Chemical Modeling of Aqueous Systems II (eds. D. Melchior and R.L. Bassett), ACS Symposium Series No. 416, American Chemical Society, Washington, pp. 212-225.

- Stengele R. H. , and Köhler S., 2001. *Permeable Reactive Barriers (PRBs) at Great Depth – Material Testing and Application.* Proc. International Containment Conference and Remediation Technology, 10-13 June, Orlando, Florida.

- Stumm W. , and Morgan J.J. , 1996. *Aquatic chemistry (3rd Edition).* New York, Wiley, pp. 1022.

- Suraci P., 2011. *Studio sperimentale dell'efficienza di barriere permeabili reattive per la bonifica di acque di falda contaminate da metalli pesanti.* Ph. D. Thesis in Geotechnical Engineering in The Mediterranean University of Reggio Calabria.

- Vikesland P., Klausen J., Zimmermann H., Roberts L.A., Ball W.P., 2003. *Longevity of granular iron in groundwater treatment processes: changes in solute transport properties over time.* Journal of Contaminant Hudrology, 64 (1-2), pp. 3-33.
- Wanner C., Eggenberger U., Mäder U., 2011. *Reactive transport modelling of Cr(VI) treatment by cast iron under fast flow conditions.* Appl. Geochem., in press, doi: 10.1016/j.apgeochem.2 011. 06.015.
- Wantanaphong J., Mooney S.J., Bailey E.H., 2006. *Quantification of pore clogging characteristics in potential permeable reactive barrier (PRB) substrates using image analysis.* J. Contam. Hydrol., 86 (3-4), pp. 299-320.
- Warner S.D. , and Sorel D., 2003. *Ten years of permeable reactive barriers: Lessons learned and future expectations.* In: Chlorinated Solvent and DNAPL Remediation: Innovative Strategies for Subsurface Cleanup, S.M. Henry and S.D. Warner, eds. ACS Symp. Ser. 837, American Chemical Society, Washington, DC, pp. 36–50.
- Wilkin R.T., McNeil M.S., 2003. *Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage.* Chemosphere 53 (7), pp. 715–725
- Wilkin R.T., Su C.M., Ford R.G., Paul C.J., 2005. *Chromium-removal processes during groundwater remediation by a zero-valent iron permeable reactive barrier.* Environmental Science and Technology, 39 (12), pp. 4599–4605.
- Zhao Y., Ren H., Dai H., Jin W., 2011. *Composition and expansion coefficient of rust based on X-ray diffraction and thermal analysis.* Corros. Sci., 53 (5), pp. 1646–1658.