

Preliminary Tests Concerning Zero-Valent Iron Efficiency in Inorganic Pollutants Remediation

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Abstract: Problem statement: This study was aimed to a preliminary evaluation of the applicability of granular Zero-Valent Iron (ZVI) to the on site remediation of groundwater polluted by inorganic contaminants by means of a Permeable Reactive Barrier (PRB). A particular interest was devoted to groundwater impacted by Acid Mine Drainage (AMD) that was caused by the oxidation of metal sulphide minerals contained in mine wastes, especially iron disulphide pyrite. Although AMD consequences were particularly evident in surface waters, the percolation through mine wastes may heavily alter the groundwater quality, therefore is particularly important the development of a restrained cost remediation technique for groundwater polluted by AMDs. **Approach:** In this study the degradation efficiency of Brown size 8/50 ZVI (Peerless Powders and Abrasive Inc., Detroit, US) was evaluated performing a leaching column test and analyzing the Oxidation Reduction Potential (ORP), metals, nitrates, chlorides and sulphates profiles along the column. **Results:** This test allowed simulating the solid-liquid contact characteristic of a real PRB behavior that proved to be a possible solution for the remediation of inorganic pollutants in groundwater. **Conclusion:** The considered material showed efficiency above 99% in metals removal, although further tests, involving biotic processes and more reducing conditions, are necessary to improve the degradation of sulphates and nitrates.

Key words: Zero-valent iron, permeable reactive barrier, acid mine drainage, groundwater remediation

INTRODUCTION

The origins of Acid Mine Drainage (AMD) are well known: pyrite and other sulphide minerals, exposed to an aquatic environment in presence of oxygen and oxidising bacteria produce heavily acidic solutions containing heavy metals and sulphates, that may produce the disappearance of aquatic life, a rust coating in river bottoms and pH values non tolerable by most crops and fauna. Typical AMD compositions, deriving from sulphide and coal mines are shown in Table 1^[1]. A surface water impacted by AMD is identified by a low pH, typically between 2 and 4 and a high concentration of iron, sulphates, Total Dissolved Solids (TDS) and heavy metals. Otherwise groundwater impacted by AMD is typically less acidic and more reducing because of the buffering influence of hydroxide, carbonate and alumino-silicate minerals occurring in aquifers and due to the consumption of dissolved oxygen and the exclusion of air in subsurface environments.

Table 1: Chemical composition of the polluted aqueous phase employed in this study (referred as column inflow) compared to some AMDs

Parameter	Coal mines AMD*	Fe-Cu-Pb-Zn sulphide mines AMD*	Column inflow
pH	2.6-6.3	2.0-7.9	2.600
ORP (mV)			642.000
Al (mg L ⁻¹)	1-58		6.100
Ba (mg L ⁻¹)			0.126
Ca (mg L ⁻¹)			249.000
Cu (mg L ⁻¹)		0.005-76	0.197
Cr (mg L ⁻¹)			0.119
Fe (mg L ⁻¹)	1-473	8.5-3200	87.000
K (mg L ⁻¹)			9.300
Mg (mg L ⁻¹)			252.000
Mn (mg L ⁻¹)	1-130	0.4	12.500
Na (mg L ⁻¹)			2040.000
Pb (mg L ⁻¹)		0.02-90	0.960
Zn (mg L ⁻¹)		0.04-1600	10.800
Cl ⁻ (mg L ⁻¹)			401.000
SO ₄ ²⁻ (mg L ⁻¹)			2614.000
NO ₃ ³⁻ (mg L ⁻¹)			1212.000

*(Gazea *et al.*^[1])

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Permeable Reactive Barriers (PRBs) are employed in a passive approach to remove inorganic pollutants from groundwater^[2]. The main challenge is actually the choice of a reactive medium that may be effectively employed in a long term remediation action and also maintains a good hydraulic conductivity. Reactive materials of possible application are essentially made of organic substance, mainly compost, or of non toxic and easily oxidizable metal, among which the most employed is Zero-Valent Iron (ZVI). In barriers rich of organic substances (i.e., wastewater treatment sludge, compost) an anaerobic biomass takes place, thus favouring the life of sulphate reducing bacteria.

Sulphides production that comes from sulphate reduction determines the abatement of heavy metals present in solution as sulphides (usually having a very low solubility) and an alkalinity enhancement.

ZVI materials are characterized by a high degradation efficiency towards heavy metals as chromium, uranium, arsenic, manganese and zinc^[3-5]. The involved removal mechanisms foresee both the adsorption on the reactive material surface and the metallic hydroxide precipitation. ZVI in contact with water and dissolved oxygen is corroded and oxidised to Fe (II) (Fig. 1 and 2) creating a reducing environment and enhancing alkalinity^[7]; moreover if proper pH and ORP conditions happen (Fig. 2), ferrous ion may be further oxidised to Fe (III). Many dissolved species,

such as carbonic acid, bicarbonates and sulphates may accelerate ZVI corrosion (Fig. 1)^[8-12]. Carbonates coming out from the above mentioned reactions generate insoluble precipitates with some metallic ions, such as iron, calcium and magnesium: Moreover, in consequence of the pH enhancement due to corrosion reactions happening on the reagent substrate, some metallic ions in aqueous phase, eventually deriving from the reagent substrate, may precipitate as hydroxides^[13]. Such hydroxides, precipitating on the reagent material surface, form a protective layer that prevents a further oxidation.

The above described processes have a negative influence on ZVI PRBs efficiency: pH increase and reagent material corrosion are intensely accelerated if groundwater has a high content of dissolved salts. Therefore, particularly in a long term, the PRB effectiveness decreases mainly because of the following two aspects:

- Iron corrosion implies a macroscopic dissolution of the metal, thus decreasing the surface area available for the contaminated plume passing through the reactive medium
- An extensive hydroxide layer prevents iron oxidation, thus decreasing the reactive material efficiency

Moreover a ZVI PRB determines important changes in the groundwater physic-chemical properties, thus producing a heavy modification of its chemistry:

- The pH increase, influencing the formation equilibria of the hydroxides of many metals, eventually released by the reagent material
- The ORP decrease, involving the creation of a reducing environment and affecting the formation equilibria of metallic sulphides

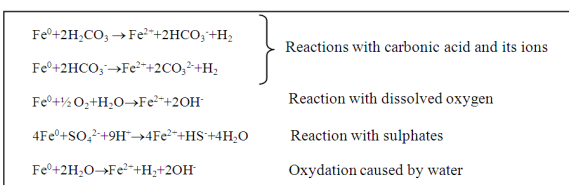


Fig. 1: Some reactions due to groundwater chemistry involving ZVI corrosion

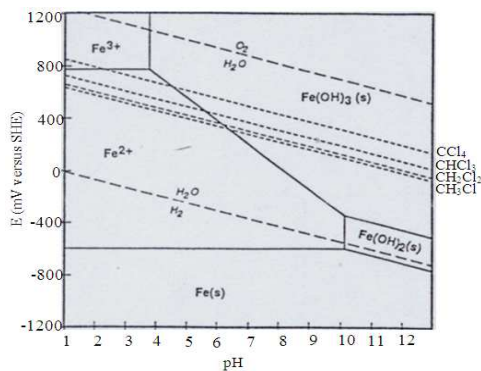


Fig. 2: Eh/pH diagram concerning Fe^0 - H_2O system at $15^\circ C$ ^[6]

The processes concerning the pollutants removal efficiency and the effects on pH, ORP and the groundwater composition should be considered in the evaluation of the potential of a ZVI material for the remediation of a AMD polluted site. Careful laboratory tests should be devoted to the study of pollutants degradation kinetic aspects, to the estimate of the PRB thickness necessary to remove all the contaminants and to the evaluation of the eventual impact of the ZVI material on groundwater.

The removal efficiency of a granular ZVI material (Brown size 8/50, Peerless Powders and Abrasive Inc., Detroit, US) towards the typical pollutants of a AMD is tested in this preliminary study, to evaluate the

applicability of a ZVI PRB for the remediation of a AMD contaminated site located in central Italy. ORP, pH, metals (Al, Ba, Ca, Cu, Cr, Fe, K, Mg, Mn, Na, Pb, Zn), nitrates, chlorides and sulphates values were monitored during a leaching column test performed employing an aqueous phase reproducing the groundwater composition of the considered polluted site. The aqueous phase was sampled at different distances from the column head after the achievement of steady state conditions and the fluido-dynamic parameters were gathered during a tracer test performed immediately after the sampling operations.

MATERIALS AND METHODS

AMD solution and reagent material: The aqueous phase employed in the column test (60 l) was prepared adding 96% H₂SO₄ until pH 2.6 to a 0.10 M Na₂SO₄, 0.2 M Fe(NO₃)₃, 0.05 M Al(OH)₃ solution. Solutions of the different metals were prepared from their salts (Sigma-Aldrich) and added to the aqueous phase. The chemical composition of the obtained AMD solution, compared in Table 1 with other AMDs^[1], was experimentally verified as described below.

The ZVI material (Brown size 8/50, Peerless Powders and Abrasive Inc., Detroit, USA) was characterized by means of particle-size and chemical analyses (Table 2). The chemical characterization of the reagent material was performed by means of an acid digestion in a Milestone 1200 Mega microwave oven with 32% HCl and 65% HNO₃. The carbon content was determined by means of a Carlo Erba CHNS-O Elemental Analyzer EA 1108.

Experimental test setup: The test was carried out in a Perspex cylinder (1 m length, 4·10⁻² m internal diameter), filled with 2.5·10⁻² m of fine gravel, 95.0·10⁻² m of ZVI material and 2.5·10⁻² m of fine gravel. The column is equipped with 8 sampling ports at the distance of 5·10⁻³, 8·10⁻², 2.05·10⁻¹, 3.55·10⁻¹, 5.05·10⁻¹, 6.55·10⁻¹, 8.05·10⁻¹, 9.30·10⁻¹ m from the beginning of the reagent substrate. The liquid phase was fed upwards by means of a ISMATEC ISM 827 with a flow rate of 0.06 l h⁻¹, with reference to the considered polluted site. The sampling operations were performed after the flow of 70 pore volume (about 5 weeks from the start) and the steady state conditions were verified by means of a tracer test. Five mL of aqueous phase were sampled by means of a glass syringe, respecting the column flow rate, from each sampling port and also the inflow and outflow were collected.

Table 2: Brown size 8/50 ZVI characterization

Parameter	New reagent
Ba (mg kg ⁻¹)	<2
Ca (mg kg ⁻¹)	175
Cu (mg kg ⁻¹)	2147
Cr (mg kg ⁻¹)	505
Fe (%)	83
K (mg kg ⁻¹)	<2
Mg (mg kg ⁻¹)	61
Mn (mg kg ⁻¹)	3760
Na (mg kg ⁻¹)	319
Pb (mg kg ⁻¹)	87
Zn (mg kg ⁻¹)	29
C (%)	2.7
bulk density (kg L ⁻¹)	2.71
specific surface area (m ⁻¹)	1.90
D ₁₀ , D ₃₀ , D ₅₀ (mm)	0.30, 0.65, 0.85

Tracer test: The test, performed immediately after the sampling operations by means of a 0.0125 M KCl solution, allowed the confirmation of the steady state conditions and the achievement of the hydrodynamic parameters of the column (D_L = 0.23 10⁻⁶ m² sec⁻¹, η_{eff} = 0.63, v_e = 2.1 10⁻⁵ m sec⁻¹). The researchers described the tracer test procedure in a previous study^[14].

Chemical analyses: Metals (Al, Ba, Ca, Cu, Cr, Fe, K, Mg, Mn, Na, Pb, Zn), nitrates, chlorides and sulphates contents were analysed employing reference procedures^[15]. A Perkin-Elmer Optima 2000 ICP-OES was employed for the metals analysis and a UV-Visible Unicam Helios α spectrometer was used for the ions.

RESULTS

The results of Brown size 8/50 ZVI material characterization are schematized in Table 2.

The profiles of ORP and pH, nitrates, sulphates and chlorides and of some metals (aluminum, copper, chromium, iron, lead, manganese, nickel and zinc) along the column, obtained considering a mass balance equation of a plug flow reactor and assuming a first order kinetic^[14] are plotted in Fig. 3-5 as a function of the residence time, obtained for each sampling port by multiplying the distance from the beginning of the reagent substrate for the aqueous phase seepage velocity (i.e., t = 0 corresponds to the first sampling port).

The chemical composition of the inflow and the outflow of the column are compared with Italian law (D. Lgs 152/2006) requirements in Table 3.

Table 3: Chemical composition of the column inflow and outflow and Italian law limits (D Lgs 152/2006) concerning groundwater

Parameter	Column inflow	Column outflow	Italian law limits
pH	2.60	9.49	5.5-9.5
ORP (mV)	642	192	-
Al (mg L ⁻¹)	6.1	<0.003	1
Ba (µg L ⁻¹)	126	<13	20000
Ca (mg L ⁻¹)	249	243	-
Cu (µg L ⁻¹)	197	63	100
Cr (µg L ⁻¹)	119	<7	2000
Fe (mg L ⁻¹)	87	<0.0005	2
K (mg L ⁻¹)	9.3	15.1	-
Mg (mg L ⁻¹)	252	296	-
Mn (µg L ⁻¹)	12500	24.7	2000
Na (mg L ⁻¹)	2040	2100	-
Pb (µg L ⁻¹)	959	<4	200
Zn (µg L ⁻¹)	10800	<2	500
Cl ⁻ (mg L ⁻¹)	401	629	1200
SO ₄ ²⁻ (mg L ⁻¹)	2614	1628	250
NO ₃ ⁻ (mg L ⁻¹)	1212	808	88

Table 4: First order kinetic constant values calculated from the column test results

Pollutant	k (sec ⁻¹)
Al	5.0 · 10 ⁻³
Fe	2.7 · 10 ⁻⁴
Mn	1.2 · 10 ⁻⁴
Zn	5.6 · 10 ⁻⁴
Pb	1.0 · 10 ⁻⁴

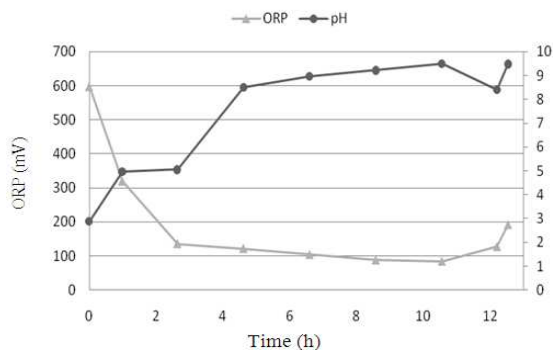


Fig. 3: ORP and pH profiles along the column

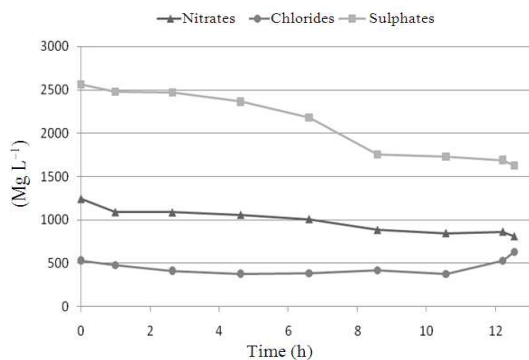


Fig. 4: Nitrates, sulphates and chlorides profiles along the column

The first order kinetic constants values calculated from the experimental results considering the removal of aluminum, iron, lead, manganese and zinc from the polluted aqueous phase are displayed in Table 4.

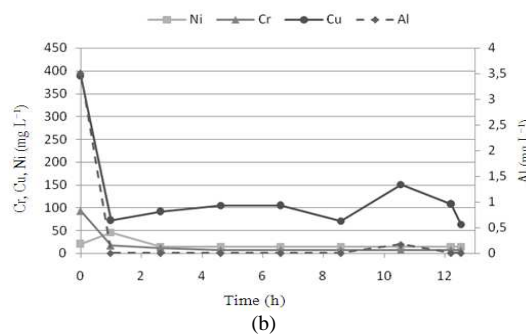
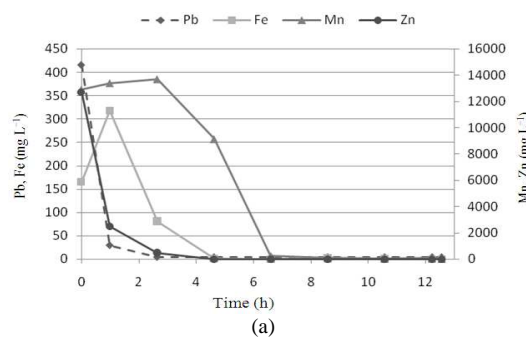


Fig. 5: Metals profiles along the column (a): Pb, Fe, Mn and Zn; (b): Al, Ni, Cu, Cr

DISCUSSION

The tested ZVI reagent substrate shows the typical composition of a cast iron material (Table 2) and it is made of scraps having dimensions between 0.12 and 1.2 mm (particle-size curve not shown).

All the outflow parameters (Table 3), nitrates and sulphates excepted, fulfill the requirements of Italian law concerning groundwater.

ORP and pH profiles along the column (Fig. 3) show a pH increase and a ORP decrease, respectively from 2.6 pH units and 642 mV in the inflow to 9.5 pH units and 192 mV in the outflow, according to the corrosion processes involving ZVI connected with the removal of metals and the contact with water (Fig. 1). The slope of both profiles rises after the sampling port No. 2 (at 0.075 m height of the reagent material column, corresponding to a residence time equal to 0.99 h in the considered boundary conditions). The highest pH value

and the lowest ORP value are reached at the sampling port No. 7 (at 0.8 m height of the reagent material column, corresponding to a residence time equal to 10.56 h), afterwards the profiles become opposite, that is the pH decreased and the ORP increased, probably due to the formation of a layer of corrosion products which reduced the specific surface area of the reagent substrate.

Nitrates profile (Fig. 4) shows a progressive decrease, particularly after No. 2 sampling port (corresponding to a ORP equal to 320 mV, that allows nitrates reduction^[16]), but Italian law requirements are not satisfied.

Sulphates profile (Fig. 4) also shows a constant decline due to the abiotic reaction reported in Fig. 1. Actually, at the ORP values measured along the column the sulphate reduction to sulphide isn't possible. Sulphates concentration, equal to 1628 mg L⁻¹, in the column outflow doesn't fulfill Italian law requirements, although considering the real performance of a ZVI PRB the sulphates reduction processes would be considerably enhanced by the presence of an organic substrate and sulphate-reducing bacteria^[17]. The analysis of Fig. 4 experimental data allowed to calculate a first order kinetic constant value equal to 1.08 10⁻⁵ sec⁻¹, leading to a necessary thickness of the PRB equal to about 5 m, obviously not realizable, in order to obtain sulphates concentration values below Italian law requirements.

Metals profiles are displayed in Fig. 5. The iron concentration significantly increased until No. 2 sampling port (from 87 in the inflow to 318 mg L⁻¹), because of the corrosion processes linked to the metals removal and the contact with water. The ORP and pH profiles after No. 3 sampling port allow the creation of solid ferric hydroxide (see Figure 2), thus explaining the drastic further decrease of the iron concentration value. The manganese profile is similar: An initial increase until No. 2 sampling port then a drastic inversion, due to Mn(II) hydroxide formation at pH values above 8^[18].

The aluminum content, not influenced by ZVI corrosion, rapidly decreases after No.2 sampling port because of the creation of the corresponding pH and ORP values of aluminum hydroxide, probably in the gibbsite form^[18]. It is also possible that adsorption phenomena take part in aluminum removal from the aqueous phase, because Al(III) is preferably adsorbed compared to other cations having a lower charge.

Zinc, lead, copper and chromium contents, influenced by pH and ORP profiles, dramatically decrease after No. 2 sampling port due to the formation of the corresponding hydroxides and also possibly because of sorption phenomena and the creation of

mixed solid phases by means of co-precipitation processes^[16].

Sodium, potassium, calcium and magnesium profiles (data not reported) don't show any relevant variation along the column because the solubility limits of their hydroxides and carbonates are not reached during the test.

First order kinetic constant values obtained for aluminium, iron, manganese, zinc and lead from the analysis of the experimental data are reported in Table 4. The removal efficiency of Brown ZVI material follows the order Al>Pb>Mn>Fe>Zn. Considering lead, characterized the lowest kinetic constant value, a PRB thickness equal to 0.95 m was calculated as necessary to obtain the fulfillment of Italian law requirements for all the considered metals.

CONCLUSION

The evaluation of the connections between a reagent material and the groundwater chemistry and of the linked kinetic aspects is mandatory for a proper dimensioning of a ZVI PRB.

On the grounds of the obtained results, Brown size 8/50 (Peerless Powders and Abrasive Inc.) ZVI material proved its efficiency in the considered inorganic pollutants remediation. Aluminium, iron, manganese, lead and zinc were effectively removed, with percentages varying from 99.6-99.9%, by means of the creations of insoluble hydroxides and also involving adsorption processes on the negative charged surface of the substrate.

Sulphates and nitrates contents weren't lowered below Italian law requirements during the performed column test, which involved predominantly abiotic processes. In real environments, due to the naturally present bacteria and particularly in PRB containing organic material, biotic processes may lead to the desired removal of nitrates and sulphates. Further tests are necessary to evaluate these aspects and to improve nitrates and sulphates removal efficiency of the considered ZVI material.

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