CRS4 Technical Report

One dimensional model of a permeable reactive barrier for the remediation of groundwater polluted by acid mine drainage in mining sites

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Abstract

The current study was conducted to evaluate by mean of a reactive transport model a possible groundwater remediation with the use of PRB technology, in the mining area eastward of Montevecchio, located in the southwestern part of Sardinia and polluted by Acid Mine Drainage (AMD). Reactive transport modeling represents an excellent tool to analyze and quantify the different reactions and their interactions in multi-component systems during advective and dispersive transport. A one dimensional reactive transport model has been developed with the code PHREEQC (Parkhust and Appelo) to assess the efficiency, in the short and in the long period, and to estimate the longevity of a PRB composed by organic carbons, used for the treatment of mine drainage in the specific site of study. The model simulates the dissolved pollutants removal inside the reactive medium, taking into account degradation rates of organic matter, reduction of sulfates, media compositional changes, ion metal concentration, removal mechanisms of sulfates and heavy metals, precipitation-dissolution of reduced mineral phases, drop in reactivity and dissolution of organic matter. Four different simulations were performed varying the hydraulic conductivity of the reactive medium, in order to evaluate how the PRB efficiency varies in the short and in the long period, varying the reactive medium characteristics.

The simulation results put in evidence the potential of an organic carbon PRB in removing inorganic contaminants contained in acidic leachates, generated at mining sites.

The study introduces an application tool that elucidates the geochemical processes that occur in preventing the pollutants transport in a contaminated site by mean of a PRB. It could be an useful tool to support the planning phase and to establish the barrier best configuration, in the hypothesis of a future PRB installation in the site of interest.

1. Introduction

Acid mine drainage (AMD) is a pollution phenomenon that occurs in active and abandoned mining sites. It forms when sulfide minerals present in mines or in mining wastes are exposed to water and oxidizing conditions. The most important mineral associated with AMD is pyrite. The oxidation of pyrite produces acidic pore water containing high concentration of sulfates and iron dissolved in solution. A second effect that has a great environmental impact is that low values of pH increase the solubility of toxic metals that dissolve in solution. This water may infiltrate into adjacent aquifer or discharge to near surface water bodies.

The main strategies used to eliminate the risk of contaminants for soil and groundwater include destruction, alteration, extraction, or separation from environmental media and immobilization of contaminants.

Permeable Reactive Barriers (PRBs) are a passive remediation technology that can be used for prevention or clean-up of AMD-impacted groundwater, as an alternative to the established pump-and-treat technology, even in extreme environments.

They consist of a filter, composed by a reactive solid material, inserted inside a trench excavation and create a reactive treatment zone directly in the path of a dissolved contaminant plume down-gradient the source of contamination. PRBs provide treatment or removal of contaminants to acceptable levels. Treatment is achieved within or down-gradient of the barrier by physical, chemical or biological processes. As groundwater moves through the reactive materials, the physical, chemical or biological processes inside the barrier allow to treat and transform the contaminants into harmless by-products. During the design of a PRB system is very important the selection of an appropriate reactive medium, depending on the type of contaminant. It should be characterized by an adequate hydraulic conductivity, sufficient reactivity, excellent environmental compatibility, availability, low cost, and long-term stability.

The barrier can be composed by organic or inorganic material. Organic materials that can be used, which incorporate various forms of organic carbon, are: municipal compost , leaf compost, wood chip, lignin, peat, while more common inorganic materials are: fly ash, bauxite, clay, zeolite. Organic materials are generally preferred in the treatment of AMD because in these conditions an anaerobic microflora forms and promotes the formation of sulfate reducing bacteria. The reduction of H_2S originated from the reduction of sulfate ions (SO_4^{2-}) produces the precipitation of sparingly soluble iron and other metal, as sulfide minerals, characterized by a low solubility.

The aim of this work is the development of a geochemical reactive transport model in order to evaluate the efficiency of a PRB in groundwater remediation of a mining site polluted by AMD.

Reactive transport model is an innovative and versatile tool for improving conceptual models of complex systems. It represents a valuable approach to the simulation of biogeochemical

processes and physical flow in chemically complex and heterogeneous environments.. The advective–dispersive transport equations of the model are solved sequentially or simultaneously, with the mass-action and mass-balance equations for chemical reactions.

A reactive transport model has been developed with the code PHREEQC (Parkhust and Appelo) to simulate the flow of a solution contaminated by AMD through a PRB composed essentially by organic carbon and to reproduce the bio-geochemical phenomena that occur inside the barrier. The model also calculate: the required residence time inside the reactive medium, basing on the concentrations in the influent and those desired in the effluent; the thickness of the barrier according to the residence time; the possible reduction of reactivity and permeability due to the precipitation of minerals; the effective life of the system.

PHREEQC is one of the computer program for geochemical reaction modeling in common use. It is Open Source and it is downloadable from the US Geological Survey site (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/). The program is used for simulating a variety of reactions and processes in natural waters or laboratory experiments. It has the capability to perform water-rock interaction models, saturation indices and speciation calculations, distribution of aqueous species, one dimensional transport models, inverse models. PHREEQC needs an input file in which the problem is specified via keywords and associated datablocks.

The database included in the program contains thermodynamic and kinetic information related to each species and can be modified by the user.

Input data are inserted before running the program, using a script. Output files, relating to the model results, are presented as tabs.

A windows version of PHREEQC prepared by Vincent Post allows to visualize the results in a graphical form. It may be obtained free of charge from the web site http://pfw.antipodes.nl/download.html.

2. Site description

The current study was conducted to examine a possible remediation in the area eastward of Montevecchio, located in the southwestern part of Sardinia, polluted by AMD. In this site, which was one of the most important Italian mine districts, the past mining activity (1840-1990) caused an important alteration and degradation of the environmental. The main source of contamination is the Piccalina tailings impoundment, located at the head of a small alluvial valley, in which flotation wastes were stored during the mining activities. The wastes have an high content of heavy metals and a residual content of pyrite that could generate the AMD process. The low content of carbonate minerals associated with the ore comports a poor buffer capability of the geological environment and a serious contamination hazard.

The tailings impoundment contains a small aquifer, alimented by rainwater and waters from the upstream catchment, with an high content of contaminants, especially iron, zinc, lead, manganese, cadmium, nickel. Approximately 50% of the tailings leachate discharges to the surface at the base of the impoundment, while the remaining generates a plume of contaminated groundwater that flows into the adjacent alluvial aquifer.

Examining the mean values of the polluted water inside the impoundment, high concentrations of contaminants were revealed, regarding to: TDS (total dissolved solids) at 180°C which is about 4500 mg/l; sulfates with an average concentrations of 3100 mg/l ; hardness with 180 °F. The analysis of micro elements showed anomalies in the mean values of Zn (340 mg/l), Cd (0.7 mg/l); Pb (about 1.2 mg/l), Fe (80 mg/l), Ni (2.2 mg/l), and Mn (64 mg/l). The pH is between 4 and 5, indicating the presence of acid mine drainage phenomena, confirmed by the values of the net acidity, that sometimes reaches values greater than 400 (mg/l).

Studying the geology of the site, the aquifer begins at the base of the tailings impoundment and flows in the plane of Campidano. It is formed by silty-sandy alluvia and transported tailings mixed to the original soil and it is characterized by coarse grain, low-medium permeability from porosity, small thickness. It is limited in the southern part by a unit of impermeable volcanic rocks and in the northern by a screes unit that can be considered impermeable due to its high clay content. The screes unit is limited in the north by volcanic rocks. The aquifer is formed essentially by quartz rich sediments, whereas the low quantity of carbonates determines a low buffering capability and an increase of contamination hazard.

Another source of contamination that affect the plain is the flow (1.5 l s-1) from an Adit of the Piccalina mine, which collects the drainage from underground workings and the seep (0.3 l s-1) emerging at the base of the impoundment. After few hundred meters the two flows convey in an uncontaminated stream and originate the Rio Montevecchio- Sitzerri.

3. Conceptual model and thermodynamic database

A conceptual model was developed to provide the basis for the simulation. It was supposed a PRB composed essentially by organic carbon, mixed homogeneously with gravel to achieve a hydraulic conductivity at least equal to that of the aquifer, in order to avoid possible phenomena of overflow or underflow. Assessing PRB performances requires complex bio geochemical processes, kinetic and equilibrium controlled, inside a heterogeneous flow field. The simulation considers the bacterially mediated sulfate reduction by organic carbon and the removal of sulfates and heavy metals by precipitation of reduced mineral phases . The model includes advective-dispersive transport, aqueous speciation of 11 components and precipitation dissolution of 10 minerals.

The reaction sequence for the reactive barrier treatment can be expressed as described below:

The organic carbon expressed as CH_2O promotes the bacterially-mediate sulfate reduction and the production of hydrogen sulfide.

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + H_2S + 2H_2O \qquad (1)$$

The production of hydrogen sulfide in presence of dissolved metals produces the formation and precipitation of sulfide species, low soluble in solution

$$H_2S + Me^{2+} \rightarrow MeS + 2H^+ \qquad (2)$$

Metals may precipitate as carbonate as pH and alkalinity raise

$$Me^{2+} + CO_3^{2-} \leftrightarrow MeCO_3 \qquad (3)$$

Accumulation of sulfide minerals within the barrier provides long term stability. The re oxidation of the minerals is limited by the availability of possible oxidizers including O_2, NO_3 and Fe^{3+}. Considering that the barrier stays below the water table, oxygen in solution is limited to aqueous solubility. Nitrate concentration in groundwater is negligible and ferric iron presence is limited by low solubility of iron oxyhydroxides.

The model also accounts for degassing reactions of CO_2 and H_2S and their loss from the domain. The reaction related to the formation of metal carbonates is reversible and in the simulation both dissolution and precipitation are allowed.

The organic carbon concentration (moles per liter) in the PRB was calculated considering a porosity of 0.38 of the reactive medium, and that 50% of the volume is composed by organic carbon while the remaining is composed by inert material (gravel).

A thermodynamic database for aqueous species and mineral solubility products adapted to this problem was prepared in PHREEQC format, arranging the MINTEQ.dat database with the geochemical reactions and the related solubility constant needed for this case of study.

A Monod equation was inserted in the database to calculate the kinetic rate of organic matter degradation mediated by sulfate reducing bacteria and the decrease in the time of the PRB reactivity:

$$Rc = \mu_{max} \left(\frac{[SO_4]}{K_c + [SO_4]} \right) \bullet mc \bullet \left(\frac{mc}{mc_0} \right) \qquad (4)$$

where:

- μmax = maximum contaminant utilization rate per mass of microorganisms (s^{-1})

- K_C = contaminant half-saturation constant (mg/L)

- $(SO4)$ = sulfate concentration (mg/L)

- mc = organic carbon content (mol/l)

- mc_0 = initial organic carbon content (mol/l)

The factor (mc/mc_0) has been added in the overall rate to account for the refractory character of organic carbon. This makes the overall rate second order with respect to organic carbon. The values related to μmax and K_C were taken from literature (Blowes and Benner).

Some solid phases were added to the database to account for the possible precipitation of metal sulfur and metal carbonates. The precipitation and dissolution of minerals are calculated by the model, using the following expression:

$$r = -k(1 - \frac{IAP}{Keq}) \qquad (5)$$

where:

- r = precipitation (r>0) or dissolution (r<0) rate

- K= kinetic constant (mol/l d-1)

- IAP = ion activity product

- Keq = solubility product

The saturation index of a phase is defined by the following equation:

$$SI = \log(\frac{IAP}{Keq}) \qquad (6)$$

A positive value of the saturation index indicates that the solution is oversaturated and the solid phases tends to precipitate, while a negative value indicates that the solution is undersaturated and the solid phase tends to dissolve. A value close to zero suggests an equilibrium condition between the solid phase and the solution.

The database was inserted in input in the model and used for the simulation.

Reaction	Stoichiometry	log Ke
Microbial reaction		
• Fe reduction	$Fe(OH)_3 + 3 H^+ + e^- = Fe^{2+} + 3 H_2O$	
• Sulfate reduction	$2CH_2O + SO_4^{2-} = 2H+ 2CO_2 + 2H_2S + 2H_2O$	
• Methanogenesis	$HCO_3^{3-} + 4H_2 + H^+ = CH_4 + 3H_2O$	
Water dissociation	$H_2O = OH^- + H^+$	-14.0
HCO3- dissociation	$HCO_3^{3-} = CO_3^{2-} + H^+$	10.329
CO2 dissolution	$CO_3^{-2} + 2 H^+ = CO_2 + H_2O$	16.681
Mineral precipitation		
• Alabandine	$MnS = Mn^{2+} + S^{2-}$	-13.0
• Millerite	$NiS = Ni^{2+} + S^{2-}$	-21.0
• Ferric hydroxide	$Fe(OH)_3 + 3 H^+ = Fe^{3+} + 3 H_2O$	4.891
• Mackinawite	$FeS + H^+ = Fe^{2+} + HS^-$	-4.648
• Hematite	$Fe_2O_3 + 6 H^+ = 2 Fe^{+3} + 3 H_2O$	-4.008
• Goethite	$FeOOH + 3 H^+ = Fe^{+3} + 2 H_2O$	-1.0
• Sphalerite	$ZnS + H^+ = Zn^{2+} + HS^-$	11.618
• Solfuro_Cd	$CdS + H^+ = Cd^{2+} + HS^-$	-14.82
• Solfuro_Pb	$PbS(s) + H^+ = Pb^{2+} + HS^-$	-14.78
• Siderite	$FeCO_3 = Fe^{2+} + CO_3^{2-}$	-10.89
• Rhodochrosite	$MnCO_3 = Mn^{2+} + CO_3^{2-}$	-11.13
• Smithsonite	$ZnCO_3 = Zn^{2+} + CO_3^{2-}$	-10.0
• Otavite	$CdCO_3 = Cd^{2+} + CO_3^{2-}$	-12.1
• Cerrusite	$PbCO_3 = Pb^{2+} + CO_3^{2-}$	-13.13
Gas dissolution		
• Carbon dioxide	$CO_2 = CO_2$	-1.468
• Water	$H_2O = H_2O$	1.506
• Oxigen	$O_2 = O_2$	-2.898
• Hydrogen	$H_2 = H_2$	-3.091
• Hydrogen sulfide	$H_2S = H^+ + HS^-$	-7.976
• Methane	$CH_4 = CH_4$	-2.850

Tab 1.Geochemical database used in the model

4. Reactive transport model

Computer modeling supplies an aid to evaluate these system that are influenced by parameters that determine the plume flow rate, metal ion properties, concentration of metal ions, properties and volume of reactive medium, presence of competitor ions. Computer models also study the factors that affect the PRB efficiency. The buffering capacity of organic carbons decreases over time because of the dissolution (consumption) of the reactive medium and the precipitation of mineral phases. As the reactive area decreases the reaction front moves forward. Input parameters are sulfates and metal load concentration, pH, Eh as pe, reactive medium characteristics (porosity, hydraulic conductivity, thickness, dispersivity)

A one-dimensional transport model was developed with the software PHREEQC in order to predict: the variation of pollutants concentration in the reactive medium along the profile of the barrier; formation of precipitates; formation of eventual gaseous phases; phenomena of degradation of organic matter; the pore water quality in the long period and the barrier longevity.

For each species i in solution, the software uses the following the advection-reaction-dispersion equation based on the conservation of mass for a chemical species that is transported in a saturated porous medium:

$$\frac{\partial C_i}{\partial t} = D_l \frac{\partial^2 C_i}{\partial x^2} - v \frac{\partial C_i}{\partial x} - \frac{\partial q_i}{\partial t} \tag{7}$$

where:

C_i = concentration of i species in solution $[ML^{-3}]$;

D_l= longitudinal hydrodynamic dispersion coefficients $[L^2 T^{-1}]$;

v = groundwater effective velocity $[LT^{-1}]$;

q_i = concentration in the solid phase (mol/kg)

The first term in the second member of the equation represents dispersive transport, the second term represents advective transport, and the third term is the change in concentration in the solid phase due to reactions (q in the same units as C). The program assumes that D_l and v are equal for all solute species, so that C can be the total dissolved concentration for an element, including all redox species. The longitudinal hydrodynamic dispersion coefficients D_l is characterized by the formula $D_l= D_e + \alpha_l{}^* v$, with D_e the effective diffusion coefficient, and α_l the dispersivity (m).

PHREEQC uses a finite difference scheme to solve the transport part of the equation, which is forward in time, central in space for dispersion, and upwind for advective transport. The modular structure of the model is considered in order to solve individually the different terms of the transport equation. The term $\delta\theta/\delta t$, representing chemical interactions for each element, is calculated separately from the transport part for each time step. This approach, known as split operator scheme, allows to separate the reactive term from the advective-dispersive. The main advantage of this technique is the great flexibility, as numerical accuracy and stability can be obtained by adjusting time step to grid size for the individual parts of the equation, whereas a disadvantage is related to numerical errors that could derive from the separation of terms, if the temporal derivation interval is not small enough.

In the realized model it was hypothesized a 5 meters thick PRB with a hydraulic conductivity of the same order of the one of the aquifer. The model domain was 10 meters long and it was formed by 20 cells of 0.5 meters each one. In the first 5 meters of domain it was represented the porous medium of the aquifer, composed essentially by quartz, while the 5 meters remaining were constituted by the PRB. A uniform and constant Darcy velocity and an effective porosity of 0.3 were used along the entire cross-section. The polluted solution inserted in the model considered the medium values obtained from the chemical composition of the water collected from two boreholes in the Piccalina tailings impoundment. Its composition is listed in table 2. Preliminary model calculation related to the distribution of species in the initial solution showed that Fe is present as Fe(3) with a concentration equal to 56 mg/l and as Fe(2) with a concentration equal to 24 mg/l, while Mn is almost completely distributed as Mn(2).

Four simulations were performed varying the hydraulic conductivity inside the reactive medium

The model allows dissolution and precipitation reactions in the porous medium of the aquifer, but does not accounts for eventual sorption reactions that could mitigate the transport of heavy metals, in order to simplify the calculation and to better evaluate the efficiency of the reactive medium in removing the contaminants.

Cauchy flux boundary conditions were used at both ends of the 1D domain. The one dimensional model simulates the profile of each pollutants contained in the solution that crosses the reactive porous medium. Another simulation performed by the model allowed to study the PRB longevity and to estimate its loss of reactivity over time, due to the dissolution of the organic matter.

The parameters that can be changed in the model to perform a sensitivity analysis are: the effective diffusion coefficient, the porosity and the hydraulic conductivity of the homogeneous mixture, the percentage of organic matter in the mixture and the maximum contaminant utilization rate per mass of microorganisms.

temp(°C)	15
pH	4.5
pe (mV)	11
temp	15.0
Cl (mg/l)	55
Ca (mg/l)	420
Fe (mg/l)	80
Mg (mg/l)	350
Si (mg/l)	21
S(6)(mg/l)	3100
Zn (mg/l)	340
Pb (mg/l)	1.2
Cd (mg/l)	0.7
Ni (mg/l)	2.2
Mn (mg/l)	64

Tab 2. Composition of the polluted solution that leachate from the Piccalina tailing impoundment

5. Results and discussions

The one-dimensional model evaluated the PRB performance simulating the changes in water chemistry as the water passes through the five meters thick PRB. Four simulation were performed, varying the hydraulic conductivity of the barrier and consequently the groundwater filtration velocity and the residence time inside the reactive medium, in order to study how the efficiency of the PRB vary with the variation of its hydraulic conductivity. The model is a useful tool to determinate if the PRB efficiency increases with the decrease of the hydraulic conductivity, as a decrease of the PRB hydraulic conductivity determines a higher residence time of the polluted solution inside the reactive medium, and to verify if a low value causes phenomena of clogging. In any case the hydraulic conductivity inside the reactive medium must be higher or at least equal compared to the aquifer hydraulic conductivity in order to avoid phenomena of underflow, overflow or that the contaminated plume turns around the PRB.

In the first simulation it was assumed a groundwater velocity inside the PRB equal to the velocity inside the aquifer that was supposed to be 20 meters per years. In the second simulation the hydraulic conductivity was increased to achieve a groundwater velocity of 30 meters per year, while in the third and fourth simulations the groundwater velocities were respectively set to 40 and 50 meters per year. The increase of the groundwater filtration velocity produced changes in penetration profiles of pollutants. The results showed that the process is more efficient diminishing the hydraulic conductivity and that a raise of the hydraulic conductivity increases the distance that metal ions travel before precipitation. In each simulation Fe(3) was completely reduced into Fe(2) in the eleventh cell (the first of treatment inside the reactive medium) because of the strongly reductive environment inside the PRB. Fe(2) concentration increased as the solution entered the barrier, because of the reduction of Fe(3), reaching a maximum value close to the entrance. In the first simulation Fe(2) decreased rapidly after it reached its maximum value, being almost completely removed in the thirteenth cell at 1.2 meters from the beginning of the PRB treatment. In the second case Fe(2) removal was achieved in the fourteenth cell at a distance of 1.7 meters from the inlet in the barrier, while in the third and forth simulation it was achieved respectively in the sixteenth and seventeenth cell. Pb, Cd, Ni and Zn have similar profiles, with a complete removal in the twelfth cell in the first simulation, in the thirteenth cell in the second one, in the fourteenth and fifteenth cell respectively in the third and fourth simulations. Mn was more recalcitrant to the treatment and precipitated more slowly than the other metals, maintaining a high concentration until the last cells. In the first simulation a satisfactory removal of Mn was achieved in the seventeenth cell, in the second simulation in the nineteenth and in the third and fourth only in the last cell. Differently from the other metals that precipitated as sulfurs, manganese precipitated almost completely as carbonate (Rhodochrosite), while only a few percentage precipitated as sulfur. Regarding to the sulfates only in the first simulation it was achieved a good removal with a final concentration of 80 mg/l, because of the high concentration in the input solution that was 3100 mg/l. In the second simulation the concentration of sulfates in the outflow solution was 480 mg/l, in the third simulation was 840 mg/l and in the fourth was 1010 mg/l. The pH reached 6.4 in each simulation with few differences in the different cases. In the first simulation the value was achieved in the fourteenth cell, while in the other three simulations it was achieved in the fifteenth cell with small variation between one case and the other. Also the redox potential (pe) showed almost the same profile in the four different cases. The initial value was 11 and it decreased rapidly in the first cell until it reached a value close to 0 and then decreased more slowly assuming a negative value, reaching -3.8 in the first simulation and -2.9 in the last one. As expectable the amount of precipitates was higher in the first simulation and it decreased increasing the hydraulic conductivity. The most abundant was sphalerite (Zn sulfur) because of the high concentration of Zn in the influent solution. Fe precipitated as mackinawite

and hematite, while Mn precipitated as carbonate (rhodochrosite). Pb, Cd and Ni precipitated as sulfur, but their contribution to the total amount of precipitates is negligible.

The model showed that in each simulation the mass loss with the organic matter dissolution was more than the mass accumulation due to precipitates and this result suggested that it is deniable the reduction of porosity and possible clogging phenomena if the hydraulic conductivity of the reactive medium is equal or higher than the hydraulic conductivity of the aquifer.

After achieving these results the one-dimensional model was implemented in order to evaluate the performances of the PRB in the long period. Four simulation were performed to study the different performances during 100 pore volume varying the hydraulic conductivity. In the first case with a hydraulic conductivity corresponding to 20 meters per year, the concentration of Fe(2) remained low for all the period considered equal to about 25 years. In the second simulation, considering a water filtration velocity of 30 meters per year, the concentration of Fe(2) started to increase after 82 pore volumes corresponding in this case to 13.7 years and reached 2.6 mg/l after 100 pore volumes (16.7 years). In the third simulation (groundwater velocity= 40 meters per year) the Fe(2) concentration was low until 72 pore volumes (9 years) and increased slowly until 80 pore volumes. Then started to increase rapidly, reaching 23.5 mg/l after 100 pore volumes. In the last simulation (groundwater velocity 50 meters per year) the PRB was efficient for the Fe(2) removal until 59 pore volumes (about 6 years) and then it started to increase, reaching high values after 100 pore volumes. Fe(3), Pb, Cd, Zn and Ni maintained low concentrations in each case until 100 pore volumes. Considering the Mn, the process was less efficient in the long period. In the first simulation its concentration started to increase after 24 pore volumes and after 89 pore volumes it was higher than the concentration in the influent solution. This fact may be explained with the dissolution of rhodochrosite, due to the reduction of pH, that caused the increment of Mn ions in solution. pH rate showed similar profile in the first three simulations, with small differences especially in the beginning pore volumes. It decreased slowly and its value was about 5.5 after 100 pore volumes in these cases. In the last simulation it showed the same behavior until 97 pore volumes and then dropped rapidly to 4.8. The pe increased lightly during the simulations and stayed negative in each cases. In the fourth simulation it raised quickly after 97 pore volume from -1.1 to -0.5 in correspondence with the drop of pH. Regarding to the concentration of sulfates, initially there are important differences in the performance of the PRB varying the hydraulic conductivity, as after few pore volumes the SO_4^{2-} concentration was less than 600 mg/l in the first simulation and more than 1900 mg/l in the fourth. Nevertheless proceeding with the simulations the differences between the four cases diminished and after 100 pore volumes the concentration of sulfates was almost the same in each simulation and it was about 2560 mg/l. The quantity of dissolved organic matter and the amount of precipitated minerals were higher in the first simulation and decreased raising the hydraulic conductivity. Considering 5 moles per liter of organic matter contained in the PRB at the beginning of the

treatment, it was reduced to 2.4 moles per liter after 100 pore volumes in the first simulation, to 2.85 moles/l in the second, to 3.2 moles/l in the third and to 3.46 moles/l in the fourth. In each simulations the quantity of dissolved organic matter was more than the precipitates amount within all the 100 pore volumes.

The results demonstrated that better performances are reached using a PRB with a hydraulic conductivity equal to the hydraulic conductivity of the aquifer. In this case the model showed that there are no risks of occlusion because the quantity of mass removed due to the dissolution of organic matter was higher than the mass accumulation caused by the precipitation of minerals. Increasing the hydraulic conductivity in the reactive medium, the efficiency of the PRB in the long period and its longevity decreased. This happened not only because of the minor residence time inside the reactive medium, but also because increasing the hydraulic conductivity increases the probability of the formation of preferential paths for the pollutants as the organic matter dissolves.

However it is preferable that the hydraulic conductivity of the PRB is not lower than the hydraulic conductivity of the aquifer in order to avoid the risk of underflow phenomena or that part of the contaminant plume turns around the barrier. Considering a PRB with the same hydraulic conductivity of the aquifer and 100 pore volumes, corresponding to 25 years, the model results indicated that the process is efficient for the removal of Fe, Zn, Pb, Cd, Ni, while it is less efficient for the Mn that is a very mobile metal, precipitates slower than the other metals and is more resistant to the treatment. The sulfates concentration maintained high values because of the high concentration in the influent solution (3100 mg/l).

6.Graphs.

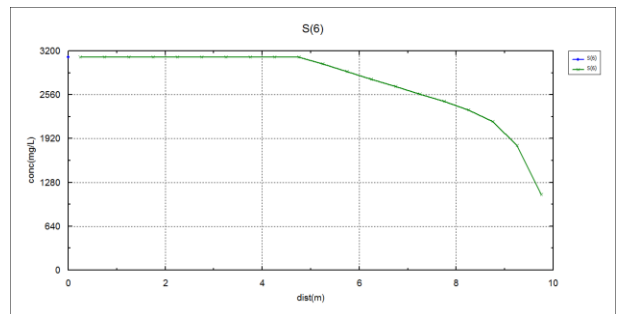## Fe(2) concentration (mg/l) profile within the domain
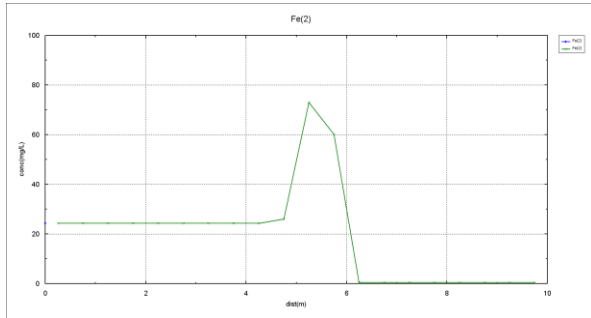
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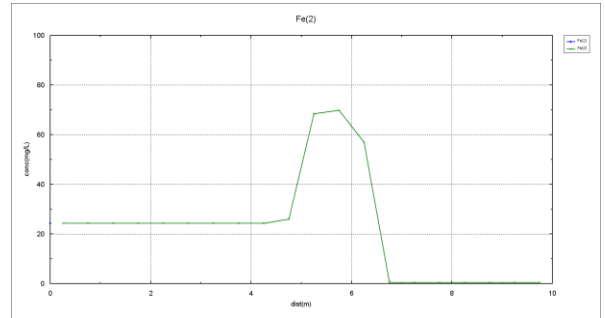
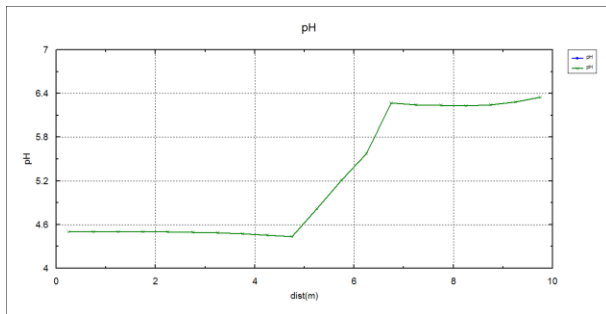Second simulation (groundwater flow velocity=30m/y)
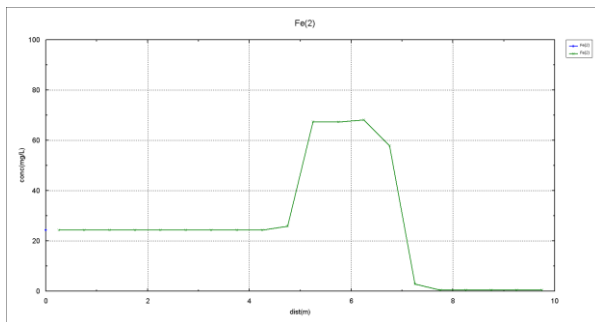
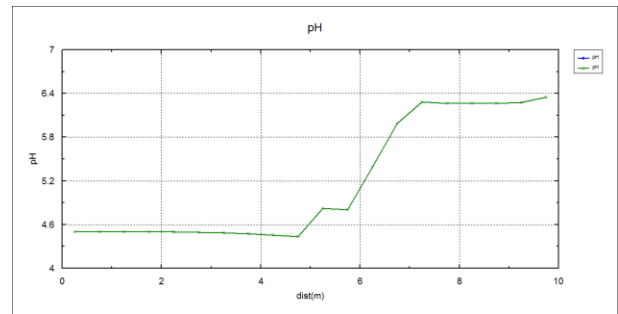Third simulation (groundwater flow velocity=20m/y)
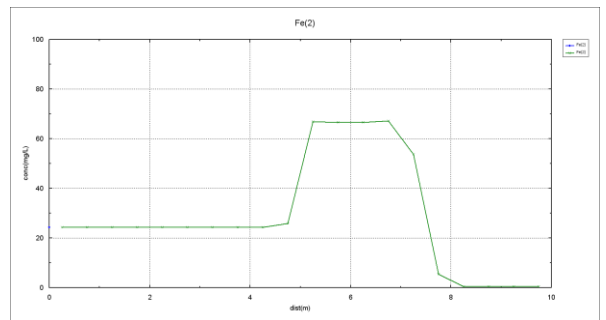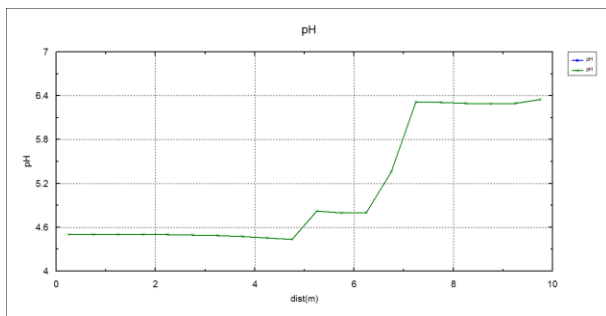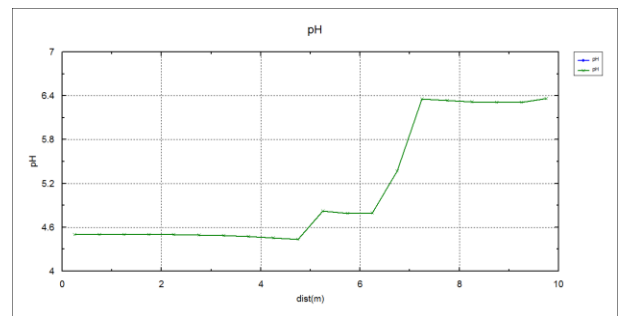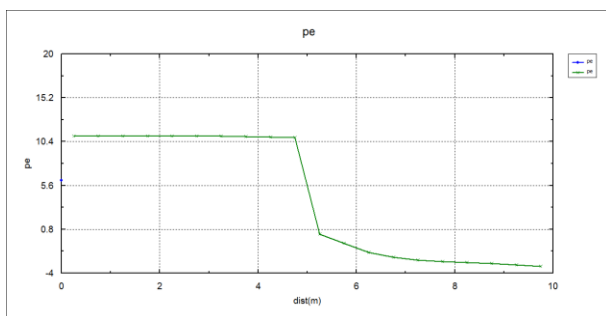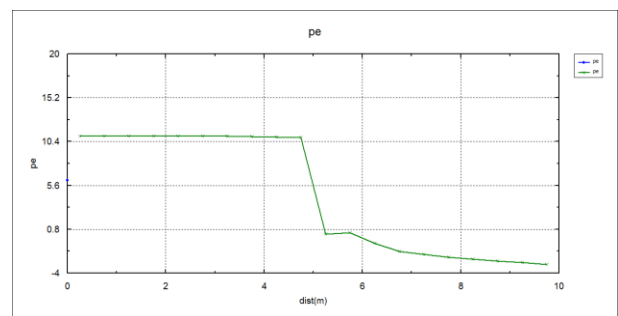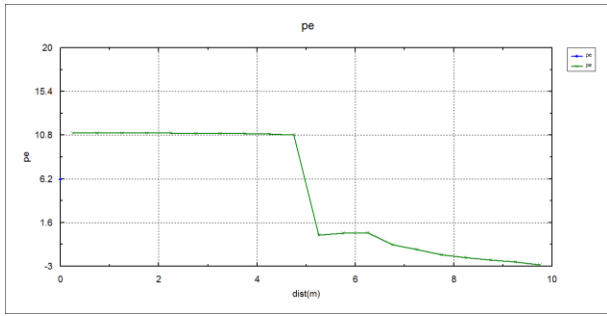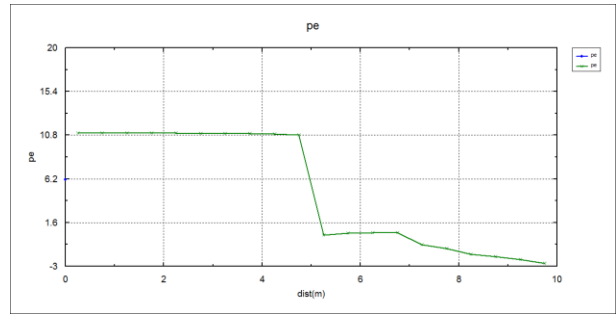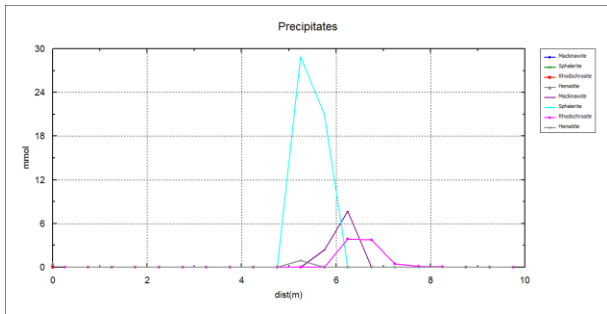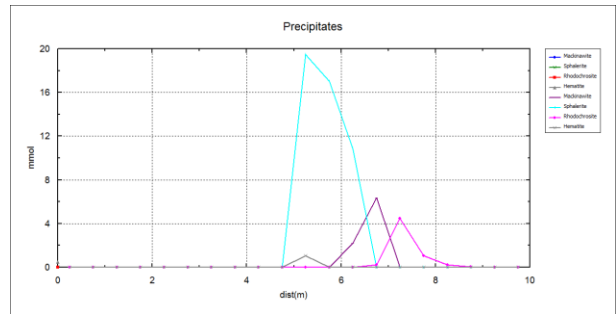

Fourth simulation (groundwater flow velocity=30m/y)

Fe(3) concentration (mg/l) profile within the domain
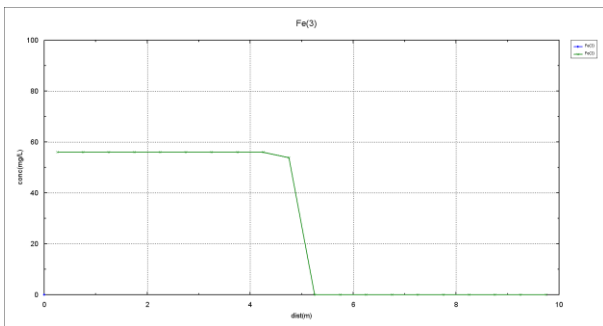
Same profile in each simulation

Zn concentration (mg/l) profile within the domain
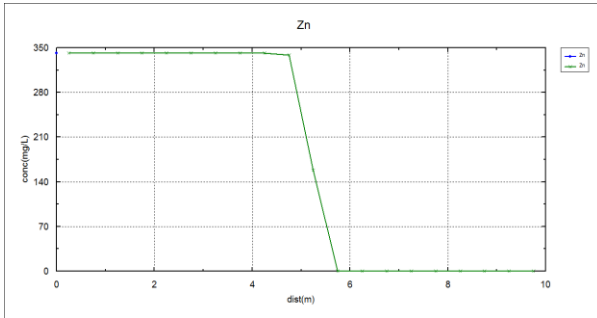
First simulation (groundwater flow velocity=20m/y)
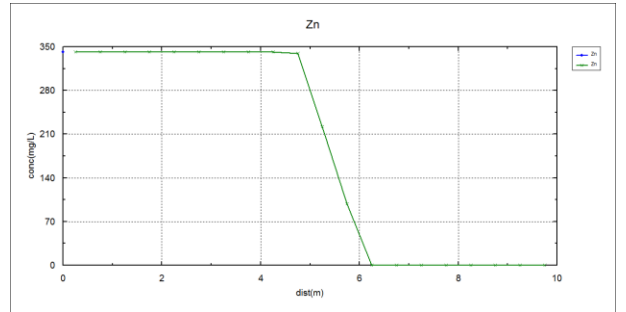
Second simulation (groundwater flow velocity=30m/y)
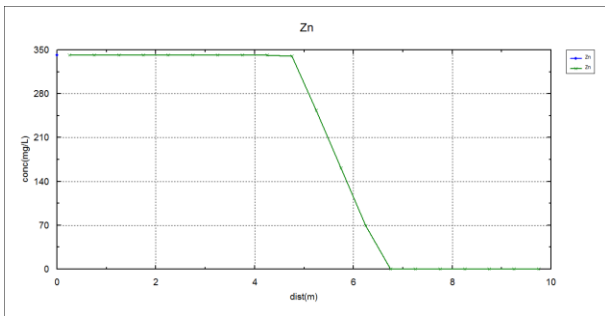
Third simulation (groundwater flow velocity=20m/y)
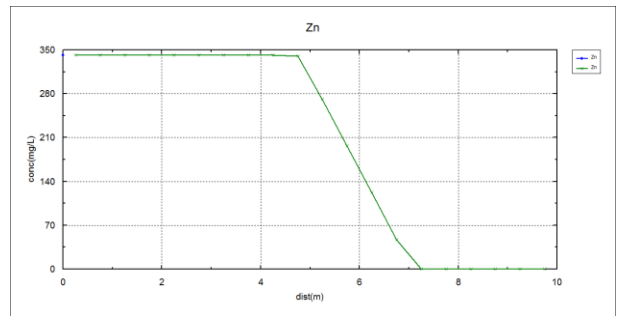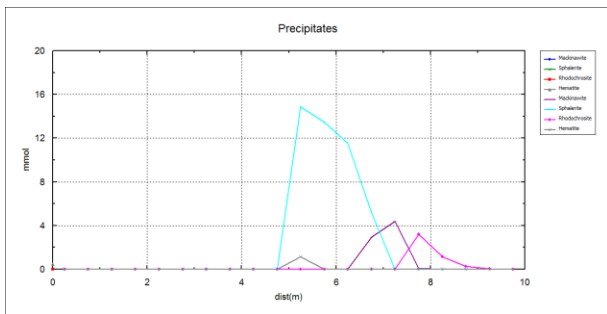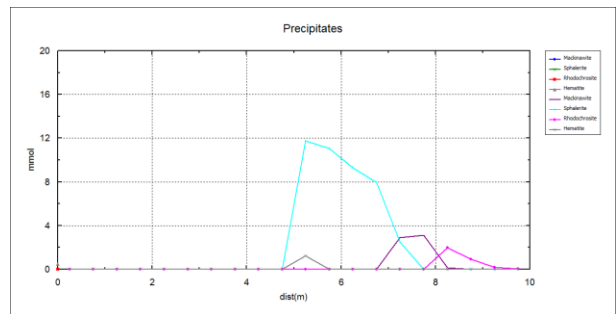

Fourth simulation (groundwater flow velocity=30m/y)

Pb concentration (mg/l) profile within the domain
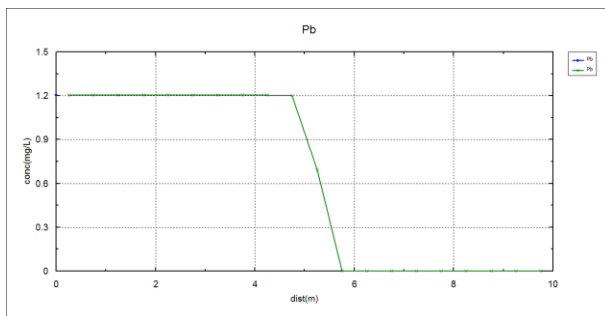
First simulation (groundwater flow velocity=20m/y)
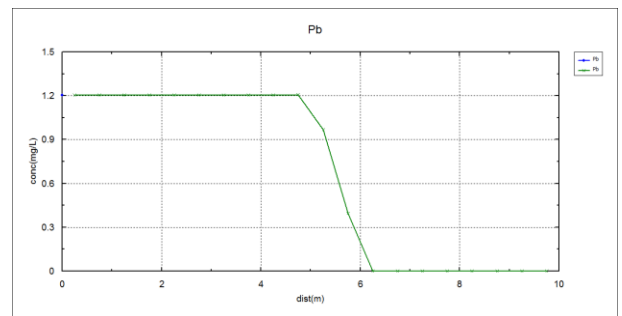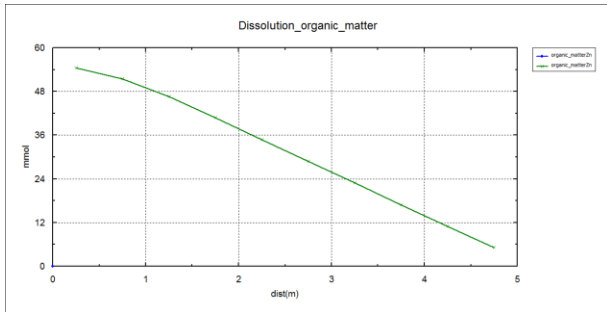

Second simulation (groundwater flow velocity=30m/y)
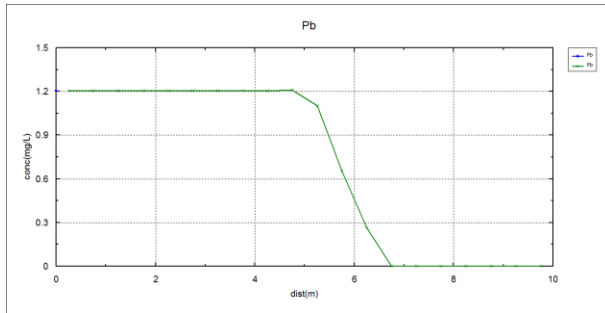
Third simulation (groundwater flow velocity=20m/y)
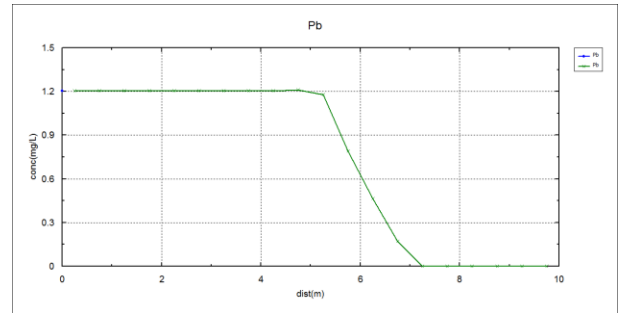
Fourth simulation (groundwater flow velocity=30m/y)

Cd concentration (mg/l) profile within the domain
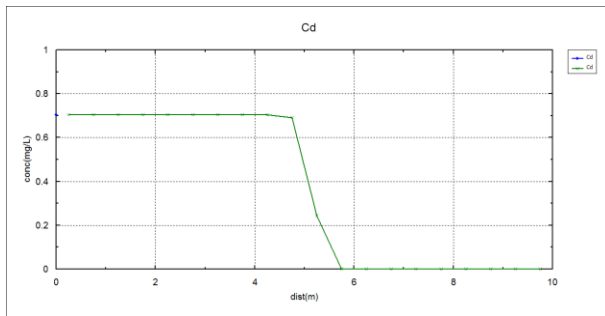
First simulation (groundwater flow velocity=20m/y)
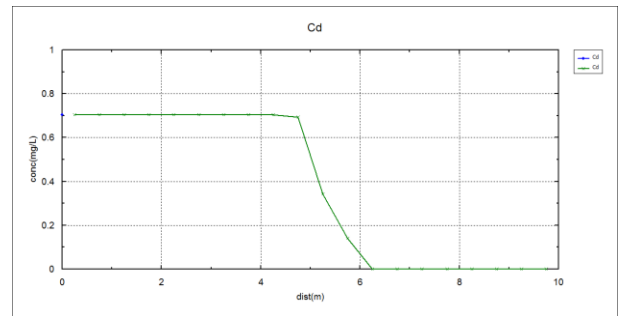
Second simulation (groundwater flow velocity=30m/y)
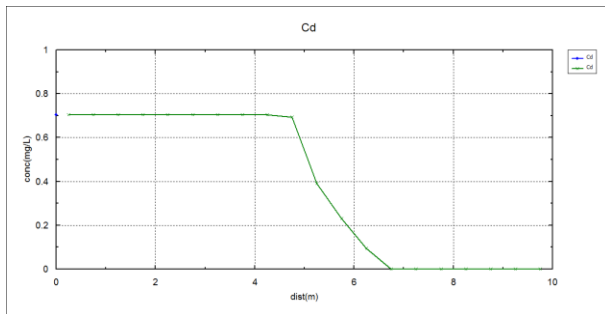
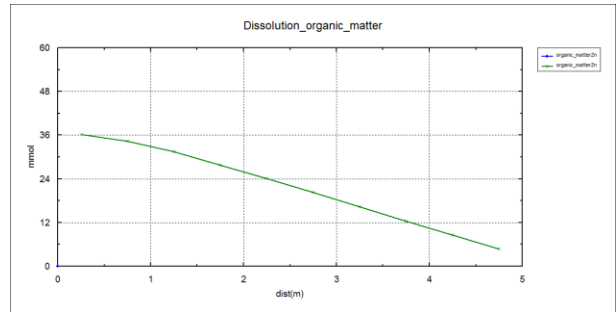Third simulation (groundwater flow velocity=20m/y)
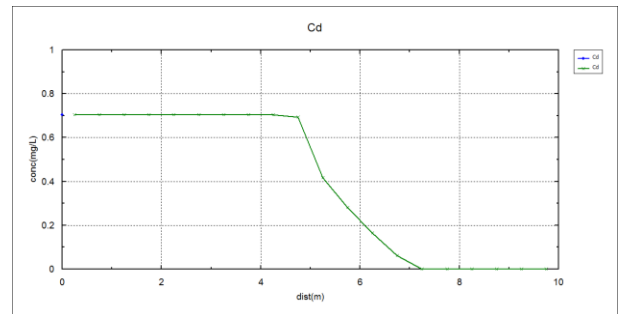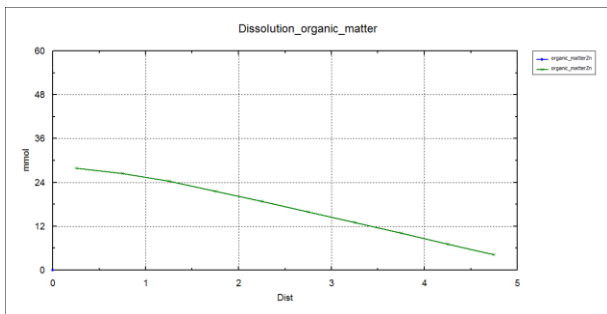

Fourth simulation (groundwater flow velocity=30m/y)

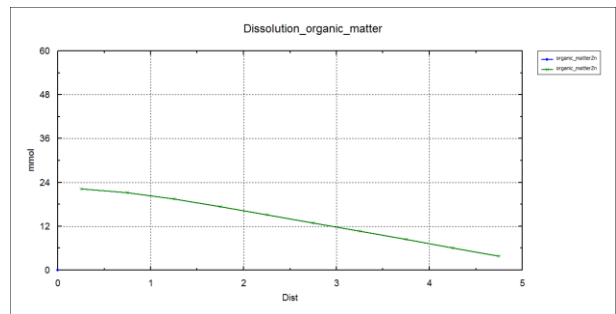## Ni concentration (mg/l) profile within the domain

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

Third simulation (groundwater flow velocity=20m/y)

Fourth simulation (groundwater flow velocity=30m/y)

Mn concentration (mg/l) profile within the domain

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

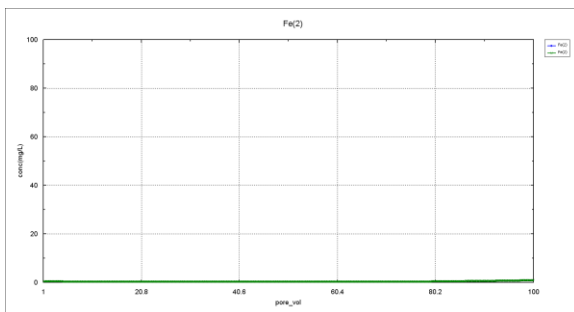Third simulation (groundwater flow velocity=20m/y)

Fourth simulation (groundwater flow velocity=30m/y)

Sulfates concentration (mg/l) profile within the domain

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

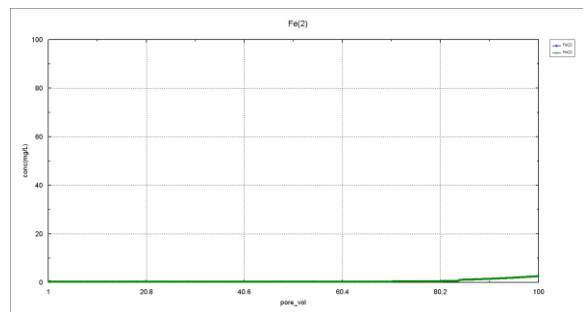Third simulation (groundwater flow velocity=20m/y)

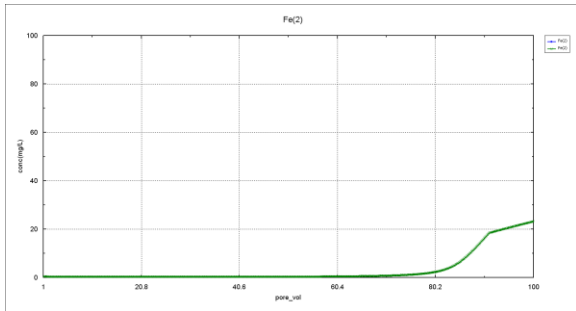Fourth simulation (groundwater flow velocity=30m/y)
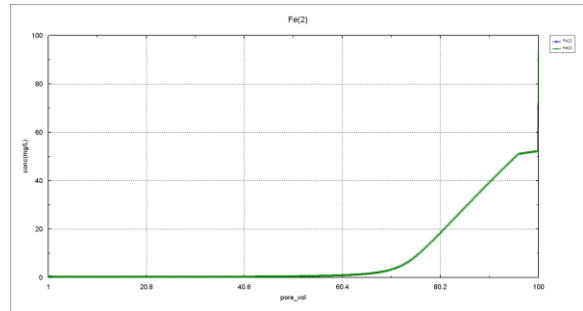
pH profile within the domain

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

Third simulation (groundwater flow velocity=20m/y)

Fourth simulation (groundwater flow velocity=30m/y)

Redox potential (mV) profile within the domain

First simulation (groundwater flow velocity=20m/y)
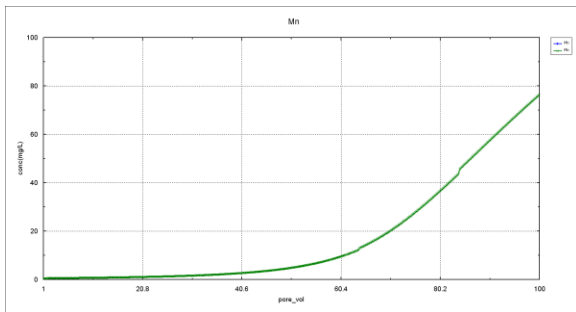

Second simulation (groundwater flow velocity=30m/y)

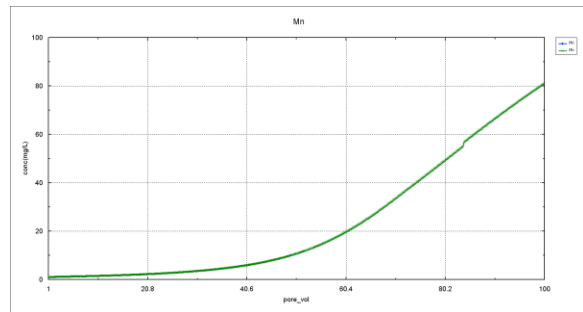Third simulation (groundwater flow velocity=20m/y)

Fourth simulation (groundwater flow velocity=30m/y)

Precipitate concentration (mmol/l) profile within the domain

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

Third simulation (groundwater flow velocity=20m/y)

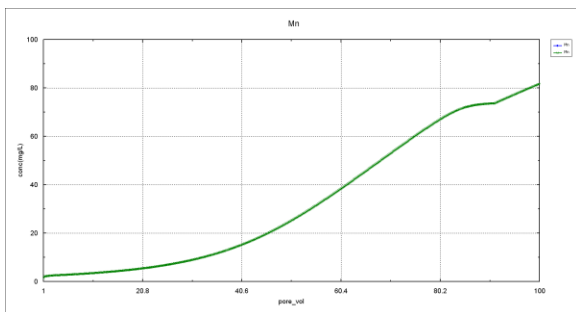Fourth simulation (groundwater flow velocity=30m/y)

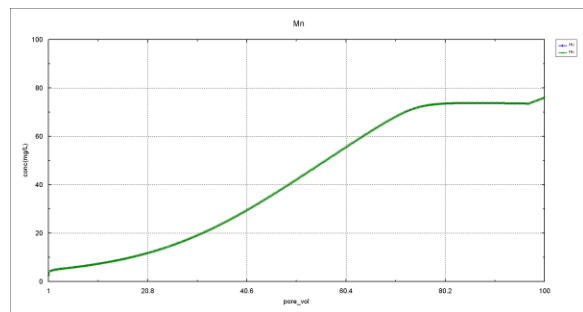## Organic matter dissolution (mmol/l) profile within the domain

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

Third simulation (groundwater flow velocity=20m/y)

Fourth simulation (groundwater flow velocity=30m/y)

Fe(2) concentration(mg/l) profile during 100 pore volumes

First simulation (groundwater flow velocity=20m/y)

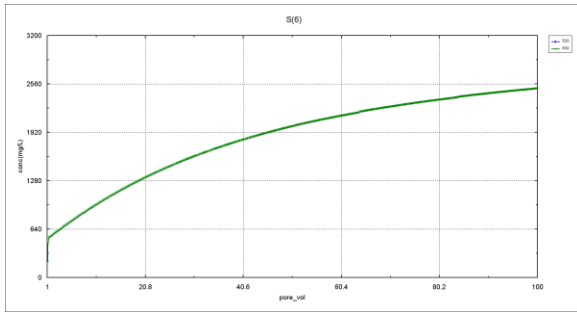Second simulation (groundwater flow velocity=30m/y)

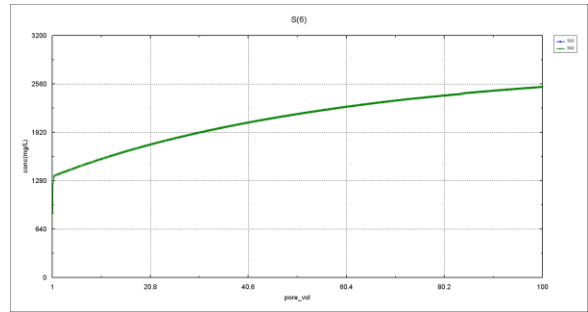Third simulation (groundwater flow velocity=20m/y)

Fourth simulation (groundwater flow velocity=30m/y)

Mn concentration(mg/l) profile during 100 pore volumes

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

Third simulation (groundwater flow velocity=20m/y)

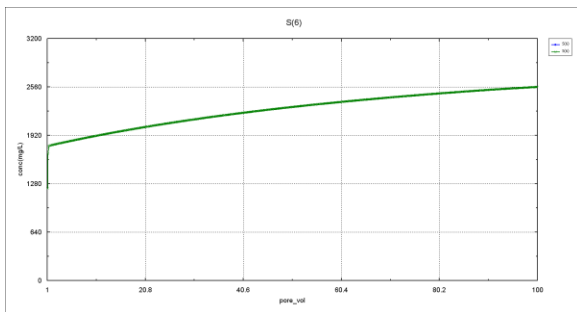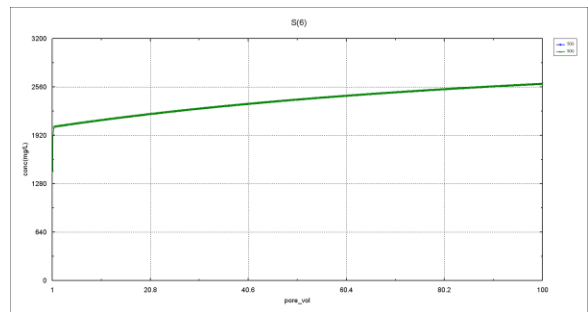Fourth simulation (groundwater flow velocity=30m/y)

Sulfates concentration (mg/l) profile during 100 pore volumes

First simulation (groundwater flow velocity=20m/y)

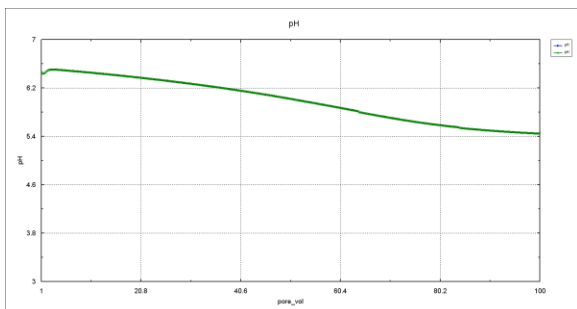Second simulation (groundwater flow velocity=30m/y)

Third simulation (groundwater flow velocity=20m/y)

Fourth simulation (groundwater flow velocity=30m/y)

pH profile during 100 pore volumes

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

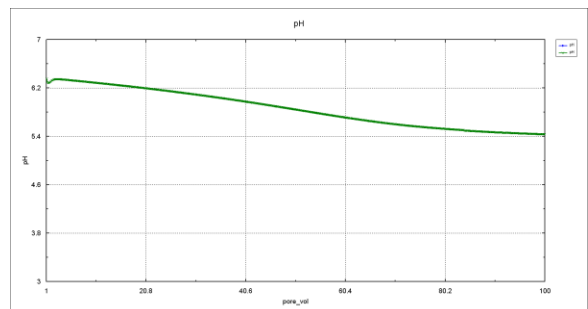Third simulation (groundwater flow velocity=20m/y)
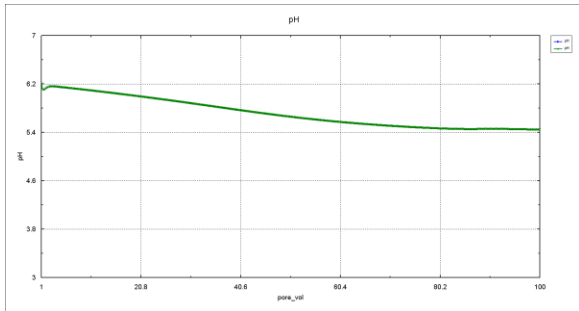

Fourth simulation (groundwater flow velocity=30m/y)

Redox potential (mV) profile during 100 pore volumes
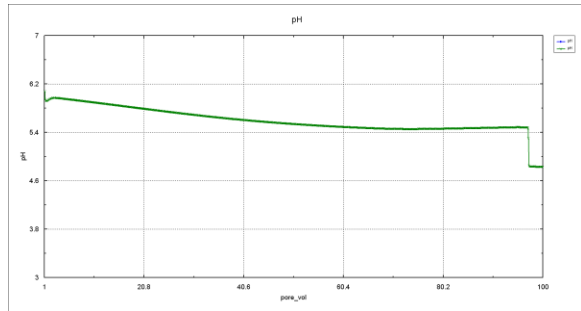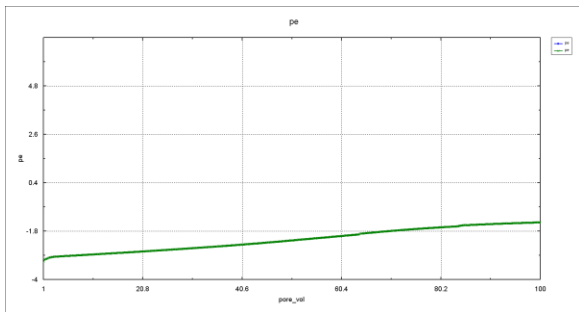

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)

Third simulation (groundwater flow velocity=20m/y)

Fourth simulation (groundwater flow velocity=30m/y

Organic matter profile (moles) profile during 100 pore volumes

First simulation (groundwater flow velocity=20m/y)

Second simulation (groundwater flow velocity=30m/y)
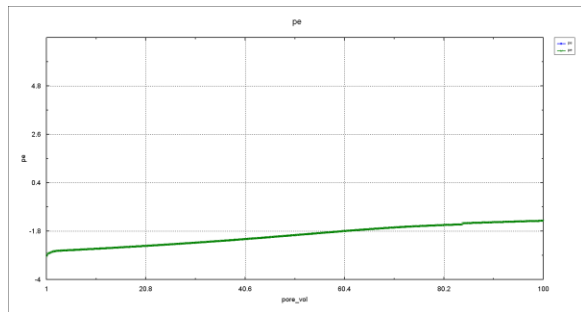

Third simulation (groundwater flow velocity=20m/y)

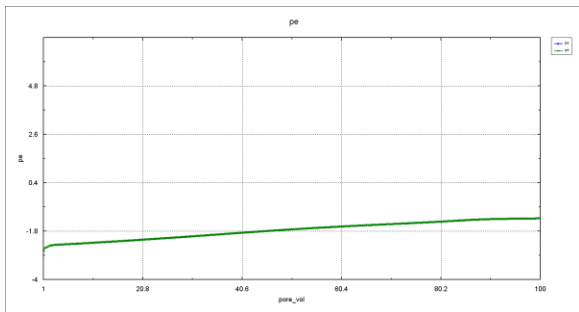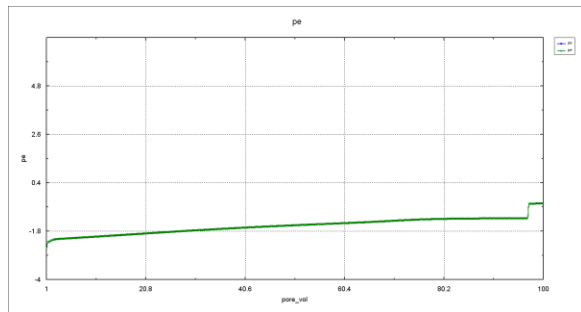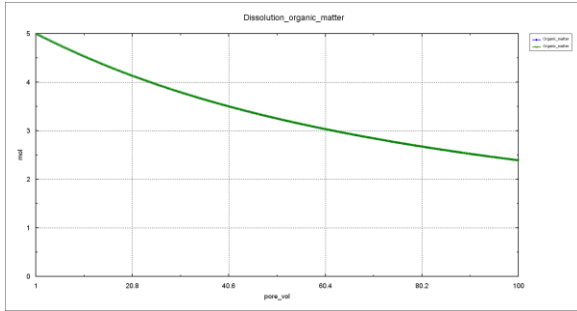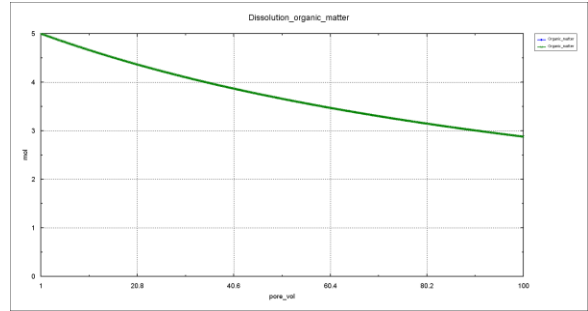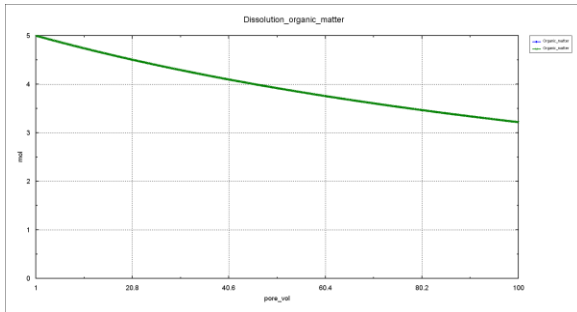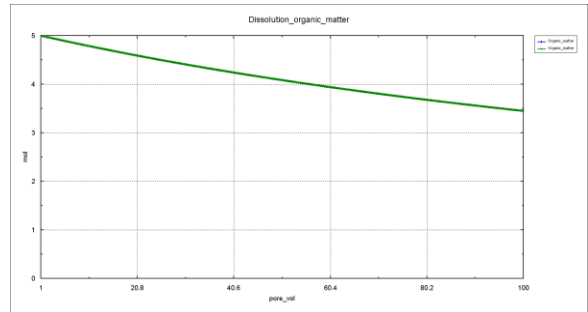Fourth simulation (groundwater flow velocity=30m/y)

7. Conclusion

Reactive transport modeling represents an excellent mean to analyze and quantify the different reactions and their interactions in multi-component system during advective and dispersive transport. Simulated modeling provides a useful tool to assess the efficiency in the short and in the long period of a PRB used for decontamination of an acidic groundwater loaded with heavy metal ions and sulfates and to estimate its longevity. In order to guarantee an accurate modeling of such system it is required a good knowledge regarding to the reaction considered, phases equilibria, reaction kinetics, speciation of heavy metals, precipitation and dissolution of minerals, loss of hydraulic conductivity due to formation of precipitates. The software PHREEQC was used to develop a one dimensional reactive transport model in order to simulate the performances of a PRB composed by organic carbons in the treatment of acidic groundwater that leachates from the Piccalina tailing impoundment in the mining area of Montevecchio, in Sardinia. A detailed geochemical model was included in the transport simulation. The model simulated interactions between solid phases and aqueous species, dissolution rate of organic matter, the progress of the reaction front inside the reactive medium. Results could be taken in account in the hypothesis of a future PRB installation in the site of Montevecchio to establish its best configuration. The model can utilize variable input such as the composition of the reactive medium and the influent polluted solution. It can be also used as a sensitivity tool to evaluate how modifications of the field parameters such as hydraulic conductivity may affect the efficiency of the process. The model can be applied to a variety of cases related to pollution generated by mining activities and treatment systems.

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