Smart barrier design for groundwater remediation

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2011 Pan-Am CGS
Geotechnical Conference

ABSTRACT

Contaminant transport in non-reactive porous media depends on soil and pore fluid properties. In the case of fine soils, chemical reactions, electrostatic interactions and biomediated reactions can modify the physical properties of the porous media. This work evaluates mass transport through reactive barriers, showing the relative importance of particle-fluid interactions and microorganism growth on contaminants displacement. Compacted soils samples were tested with arsenic solutions and landfill leachate as permeating liquids. The addition of clay decreased the hydraulic conductivity and delayed the contaminant displacement due to electrostatic attraction between the charged soil particles and counter ions. Microorganisms were responsible for pore clogging due to the increase of biomass with permeation time. These two effects were simultaneously considered by implementing a 1D-mass transport equation to simulate the behaviour of reactive barriers. Obtained results are of fundamental importance for the design of “smart” barriers for the remediation of contaminated groundwater.

RESUMEN

El transporte de contaminantes en un medio inerte depende de las propiedades del suelo y del fluido intersticial. Este trabajo cuantifica variables que controlan el transporte de masa através de barreras reactivas, mostrando la importancia relativa de las interacciones fluído-partícula y el crecimiento de microorganismos en el desplazamiento de contaminantes. Se analizaron muestras de suelos compactados, permeadas con una solución de arsénico y lixiviado de un relleno sanitario. El agregado de arcillas disminuyó la conductividad hidráulica y retardó el desplazamiento de contaminantes, debido a la atracción electrostática entre las partículas cargadas del suelo y los iones de intercambio. Los microorganismos fueron responsables de la oclusión de los poros, debido al incremento de la biomasa con el tiempo. Estos dos efectos fueron considerados simultáneamente implementando un modelo de transporte 1D para simular el comportamiento de las barreras reactivas. Los resultados obtenidos son de fundamental importancia para el diseño de barreras “inteligentes” para la remediación de sitios contaminados.

1 INTRODUCTION

The environment suffers a constant degradation due to natural and anthropogenic sources of contamination. In particular, several physical, chemical and biological processes develop in the soil and groundwater which modify their quality.

Groundwater quality is initially controlled by the properties of the porous media. Minerals are dissolved and/or precipitated during the flow of water in porous media, decreasing the water quality in the case that the chemical compounds are considered as harmful.

Average As concentration on Earth crust ranges from 1.5 to 2.0 mg/kg. Under certain circumstances (e.g. pH and contact time) the solid phase lixiviate As ions increasing its concentration on the pore water. An example of this situation, with a broad distribution in the central part of Argentina, is the presence of arsenic (As) in most of aquifers (Francisca and Carro Pérez 2009).

On the other hand, human contamination of natural resources and its mitigation is widely studied nowadays. With the increasing water demand and its scarcity at a surface level in many places around the world, the preservation of underground resources has become of fundamental interest. One of the many concerning sources related to contaminants infiltration is related to the final disposition or municipal solid wastes. Small volume of the leachate generated in the cells contains high concentration of contaminants, which can displace affecting soil and groundwater quality.

1.1 Contaminant transport

Diffusion, advection and mechanical dispersion are the main mechanisms responsible for the mass transport in soils. Diffusion arises when there is a spatial variability of ion concentration; advection is related to the seepage velocity and depends on the hydraulic conductivity of the porous media and mechanical dispersion is produced due to unequal pore sizes, flow paths and velocity gradient inside the soil pores (Fetter 1993).

Diffusion is frequently disregarded in the case of coarse soils, given that the effect of advection prevails when the media hydraulic conductivity is higher than 10^{-8} m/s. Nevertheless, in the case of low hydraulic conductivity liners, where the flow velocities must achieve lower values (Benson and Dwyer 2006), diffusion begins to play an important role in the contaminant transport. In many cases diffusion may even become the dominant process in mass transport inside the pores (Mitchell and Soga 2005).

In an ideal and inert porous medium, hydraulic conductivity depends on the properties of the solid phase (e.g. porosity and specific surface), and on those that are characteristic of the permeating liquid (e.g. density and viscosity). When the medium is no longer inert and interacts with the fluid and its solutes, several chemical reactions and physical phenomena may develop affecting the liquid displacement inside the pores. Physical phenomena comprise changes of the adsorbed double layer thickness and sorption of chemical compounds dissolved in the fluid. These chemical reactions may lead to the formation of precipitates. Also, the presence of microorganisms can promote biomediated reactions capable of modifying the physical properties of the porous media (VanGulck et al., 2003).

1.2 Reactive barriers

There are several alternatives for the remediation of groundwater including chemical oxidation, precipitation, coagulation, adsorption, biological degradation, permeable reactive barriers, etc (Sharma and Reddy 2004).

Reactive barriers are permeable for water but have the capacity of retaining the dissolved contaminants. Then, the contaminant concentration can be significantly reduced when groundwater passes through the barrier. These barriers can be filled with several materials depending on the chemical properties of the contaminant to be treated, and for this reason they have a large amount of applications.

Reactive barriers are divided in two categories: permeable reactive barriers (PRB) and low permeability reactive barriers (LPRB). The first ones are used with the aim of remediating a contaminant plume; whereas the second ones are used as containment barriers when low flow rate and a decrease in the contaminant toxicity are desired.

The objective of this research is to evaluate mass transport through reactive columns by simultaneously considering the influence of flow rate and retardation effects. The effects of adsorption, physical occlusion and microbiological activity on the removal of contaminants from the permeating liquid are addressed.

2 MATERIALS AND METHODS

2.1 Soils

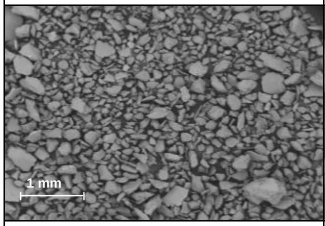
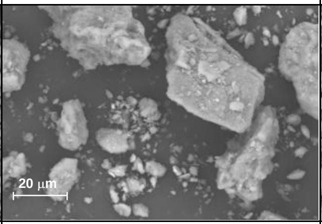
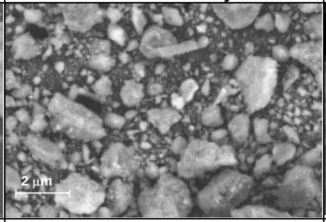
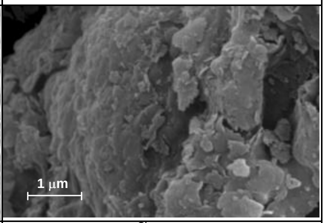
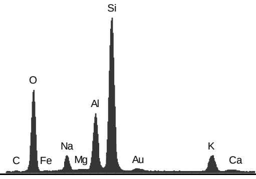
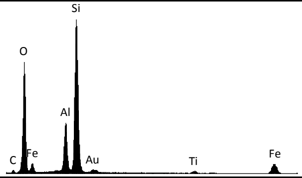
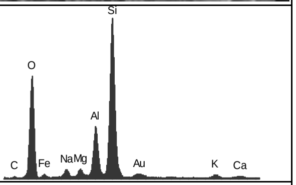
Soils used in reactive columns were sand, a residual clay, silt, and bentonite. Table 1 summarizes the main physical properties of these materials, as well as scanning electron microscopy (SEM) images and energy dispersive x-ray analysis (EDXA).

The residual clay is a lateritic soil from the Northeast of Argentine and is mainly formed by iron and aluminum oxides and hydroxides according to the EDAX analysis.

The silt is a typical soil from the Chaco-Pampean plain and covers more than 600.000 km^2 of the central part of Argentine. This soil is formed by fine sand, silt and clay particles, transported by aeolian action (Zárate 2003). The mechanical properties of this soil have been extensively studied in the past decades (Terzariol 2009) and are highly affected by moisture content, presence of rigid inclusion and stress level (Moll and Rocca 1991, Redolfi 1993, Terzariol and Abbona 1999, Clariá and Rinaldi 2000, Rocca et al. 2006, Francisca 2007, Francisca et al. 2008).

Bentonite contains more than 92% of sodium montmorillonite (data provided by manufacturer Minarmco S.A.). This mineral was extracted in the provinces of Río Negro and Neuquén, and is frequently used in landfills, slurry walls and many other geoenvironmental applications, due to its expansive characteristic and low hydraulic conductivity.

Table 1. Relevant soil properties

Sand	Loessical silt	Residual clay	Bentonite
			
N/A			
LL = N.P. PI = N.P. Part. < 74 μm = 1.28% Part. < 2μm = 0% Gs = 2.68 Ss < 0.01 m^2/g	LL = 27 % PI = 2.8% Part. < 74 μm = 96% Part. < 2μm = 4% Gs = 2.67 Ss = 2.5 m^2/g	LL = 65 % PI = 39.7% Part. < 74 μm = 100% Part. < 2μm = 66% Gs = 2.80 Ss = 3.7 m^2/g	LL = 285 % PI = 240% Part. < 74 μm = 100% Part. < 2μm = 80% Gs = 2.71 Ss = 731 m^2/g

The sand is mainly composed by silica (43%), feldspars (12%) and muscovite (1%), granite fractions (38%) and other clasts in a less percentage. This sand is the same used by Montoro and Francisca (2010) to evaluate the influence of particle-fluid interaction mechanisms on the hydraulic conductivity of granular media.

2.2 Compaction and permeating fluids

Soil columns were compacted with distilled water (DW) (electrical conductivity < 3 μS/cm). A landfill leachate (LL), a 1 mg/l arsenite solution ($[AsO_3]^{-3}$) (AS) and distilled water were used as permeating liquids. The landfill leachate was filtered with a qualitative filter paper to remove particles > 10 μm from the permeating liquids, prior to the tests.

2.3 Sample preparation and hydraulic conductivity tests

Granular materials were oven dried at 105º C. Soil mixtures were prepared by adding different amount of lateritic soil or bentonite to the silt or sand. The hydraulic conductivity was measured in rigid wall permeameters. The falling head test procedure ASTM D5856 and constant head test procedure ASTM D2434 (ASTM 2007) were used when the hydraulic conductivities were lower and higher than 10^{-8} m/s, respectively.

2.4 Arsenic determination

Arsenic was quantified with a colorimetric method. Macherey-Nagel's Quantofix® Arsenic Test Kits were used with detection range between 0.001 and 0.5 mg/l and the concentrations were determinate by means of an image digital analysis proposed by Carro Pérez (2009). With this analysis, the precision is enhanced and the appreciation errors are reduced.

3 RESULTS

3.1 High permeability soil column

A soil column was prepared with 90% sand and 10% lateritic soil. The sample achieved an average hydraulic conductivity of 1×10^{-7} m/s. This column was periodically monitored for 150 days, controlling the volume of permeating liquid and arsenic concentrations in the effluent liquid collected in the outlet port.

These results were analysed by a 1D contaminant transport model, according the dispersion-advection and dispersion-advection-retardation equations (Figure 1). From this analysis the dispersion coefficient, D^*_L, and the retardation coefficient (R) were found, being 6.5×10^{-12} m^2/s and 1170, respectively.

3.2 Low permeability soil column

Hydraulic conductivity of silt-clay mixtures was monitored during 2 years (Figure 2). When the permeating fluid is distilled water (continuous line) *k* remains approximately constant.

When LL is the permeating fluid, the hydraulic conductivity showed a strong decrease close to two orders of magnitude. A total of 10 silt-bentonite samples were permeated with the leachate lixiviate and in all cases the threshold time for the decrease of hydraulic conductivity ranged from 5 to 11 months. The reduction in the samples hydraulic conductivity is related to bacterial growth and biofilms formation (Francisca and Glatstein 2010).

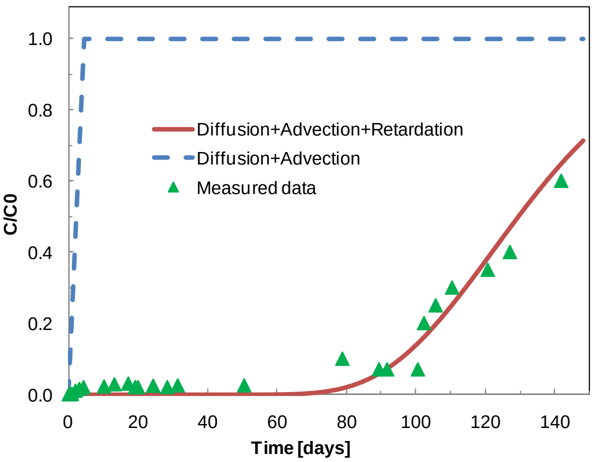


Figure 1. Arsenic concentration in the effluent liquid collected in the outlet port. Tested soil: sand-laterite (C = outlet concentration, C_0 = initial concentration).

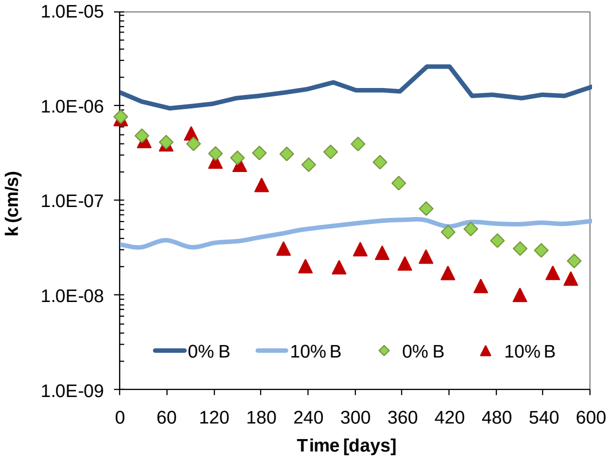


Figure 2. Long term hydraulic conductivity of silt and silt-clay mixtures permeated with distilled water (solid lines) and landfill leachate (symbols). B=bentonite content in weight by dry weight of soil.

4 DISCUSSION

The advection-dispersion-retardation model allows calculating the contaminant concentration change, according to (Sharma and Reddy 2004):

$$C_f/C_0 = \frac{1}{2} \operatorname{erfc}[(Rx - Vt)/(2(D^*_L tR)^{1/2})] \quad [1]$$

Where C_0 and C_f are the initial and final concentrations, respectively, D^*_L is the total dispersion coefficient, which computes mechanical dispersion and molecular diffusion, and V the flow velocity, R is the retardation coefficient, and t is the time of permeation.

The retardation coefficient (R) relates the time for which the contaminant concentration in the effluent is equal to $C_0/2$ in the case of reactive soils (t_2) respect to the expected time for inert soils (t_1):

$$R = t_2 / t_1 \qquad [2]$$

Contaminant concentration highly depends on flow velocity as shown in equation (1), and consequently it also depends on the hydraulic conductivity according to Darcy's law. This means that R also is highly affected by the hydraulic conductivity of the soil.

A decrease in one order of magnitude in the hydraulic conductivity promotes higher retardation factor and longer times for the contaminant percolation, as shown in Figure 3. In the simulated situation if the hydraulic conductivity decreases in two orders of magnitude the concentration in the outlet port after 10 years only reaches 30% of the initial concentration.

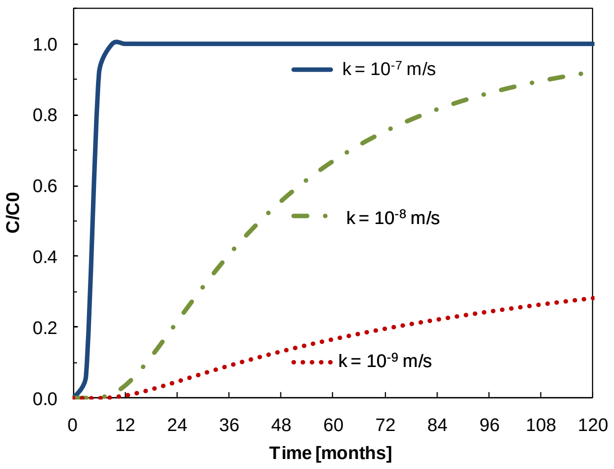


Figure 3. Influence of the time of permeation on the contaminant concentration after passing through reactive barrier with different hydraulic conductivity.

4.1 Long term *k* variation

The influence of time on the hydraulic conductivity observed in Figure 2 can be modeled as follows:

$$k_t = k_\infty + [(k_0 - k_\infty)/(1+(t/t_\alpha)^{t\alpha})] \qquad [3]$$

Where k_t is the hydraulic conductivity at the time t, and k_0 and k_∞ are the initial and final hydraulic conductivities, respectively (Figure 4).

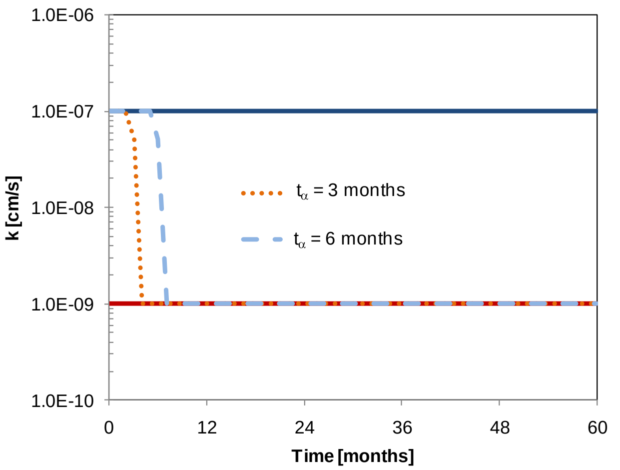


Figure 4. Theoretical variation of *k* with time according to equation 3.

This time dependence of hydraulic conductivity can be included in the mass transport equation. By coupling both models it can be noticed that the time required to reach maximum concentration levels in the effluent is significantly extended. Figure 5 shows the expected trends when *k* decays in two orders of magnitude and the threshold time is 3 and 6 months. The threshold time, initial and final hydraulic conductivity are of fundamental relevance and should be measured for each soil and permeating liquid.

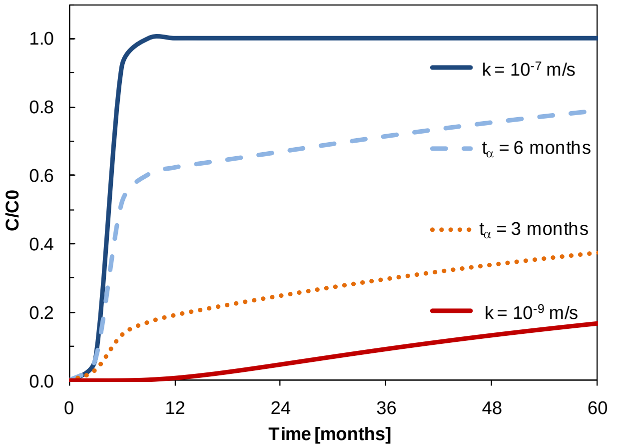


Figure 5. Theoretical variation of arsenic concentration in the effluent with the time of permeation when the hydraulic conductivity decreases from 10^{-7} m/s to 10^{-9} m/s as shown in Figure 4.

4.2 Smart barriers design

Reactive barriers are extremely versatile in terms of the granular reactive materials, the treated contaminants and the constructive configuration. According to this, the results obtained in this work could help on the design of a barrier system for which the hydraulic conductivity can be manipulated. With the aid of bacteria and the injection of nutrients microbial growth can be favoured and bioclogging mechanisms could be enhanced to reduce k (Clement et al. 1996, Francisca and Glatstein 2010). In addition, existing technologies would allow developing injection systems to return the barrier to its initial state (for example by adding antibiotics).

The design of a reactive barrier includes de calculation of its width (W), which depends on the flow velocity and the residence time (t_{res}) required to achieve the target concentration, according to the following equation:

$$W = V * t_{res} \qquad [4]$$

According to Equation 4, a decrease in the flow velocity would be reflected in a reduction in the necessary barrier width which makes the barrier less expensive. Other consequence is the possibility of using reactive materials with larger t_{res}. However, the t_{res} depends on the initial and final concentration values and on the first order decay constant (β) according to:

$$t_{res} = 1/\beta * \ln(C_0/C_f) \qquad [5]$$

Where β is related to the contaminant half-life in a given reactive material ($t_{½}$) as follow:

$$\beta = -\,0.693 \ / \ t_{½} \qquad [6]$$

Then, equations 4 and 5 confirm that when flow velocity is reduced by the injection of nutrients and microorganisms, the barrier could be filled with a low cost or less pure reactive media having higher contaminant half-life.

5 CONCLUSIONS

This research evaluates mass transport mechanisms in porous media with time varying hydraulic conductivity. Obtained results are of fundamental importance for the design of novel smart reactive barriers. The main contributions are summarized as follow:

- Contaminant transport in porous media cannot be determined by considering the soil as an inert material.
- Physicochemical interactions between soil and dissolved ions produce the retardation due to the adsorption of the contaminant.
- Presence of bacteria in the permeating liquid can be used to take advantage of the reduction of hydraulic conductivity associated to a bioclogging mechanism (Francisca and Glatstein 2010).
- New and more functional permeable reactive barriers can be developed by controlling the hydraulic conductivity with the time of permeation. In this case, less expensive smart barriers can be designed using less pure reactive materials.

ACKNOWLEDGEMENTS

This work was partially supported by SECYT-UNC and CONICET. MECP and DAG thank the support given by CONICET during this research.

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