

Clay and landfill leachate interaction: experiments and reactive transport modeling

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INTRODUCCIÓN

Landfills are the most common methods of waste disposal and generate a polluting leachate that can migrate through the soil. In order to protect groundwater and soils, clay barriers are located at the bottom of landfill areas. These clay barriers are characterised by low porosity, low hydraulic conductivity, slow diffusive transport and high capacity of cation adsorption.

The aim of this work is to evaluate the diffusion of a synthetic urban landfill leachate through compacted natural smectite-illitic clays with carbonates and sulfates and to predict the functioning of the liner under different scenarios of clay composition. Due to the complexity of coupled transport and reactions processes involved in clay barriers from landfill areas, an experiment under controlled conditions was performed in the laboratory. In order to fully understand the overall process and extract more general and quantitative laws, the results were interpreted with reactive transport modelling.

MATERIALS AND METHODS

The laboratory test was performed using Bailén clay. This material is composed by illite (33%), smectite (12%), kaolinite (7%), calcite (11%), dolomite (5%), quartz (30%) and albite (1%) and pyrite. The leachate used in this study is a saline solution characterized by high acetate content and acid pH.

The tests consist of the diffusion of the components of a synthetic acid leachate through a disc of compacted clay. The compacted clay at 90 % of water saturation, with a porosity of 0.29, was shaped into a cylindrical column (11 cm height, 7 cm diameter and 423 cm³ volume). It was inserted inside a Teflon sleeve which was covered with a steel

body to avoid clay deformation. A volume of 200 cm³ of the synthetic leachate was situated inside of another Teflon sleeve and steel cell with the same dimension than the precedent cells. Between the two cells there was a steel porous cylindrical filter in order to allow solute diffusion between leachate and clay porewater.

The system was maintained at 25°C during 77 days. Then, the compacted clay was withdrawn and cut in 5 cylindrical sections of 2 cm thickness. The samples are labeled B1 to B5 from surface to bottom. Pore waters were extracted by squeezing at laboratory conditions (pressure lower than 1MPa). The soluble ion concentration was

measured by ion chromatography.

The code RETRASO (Saaltink et al., 1998) and the wateq4f database (Parkhurst and Appelo, 1999) has been used for the diffusion-reaction calculations. The exchange coefficients for Bailén clay were modified to obtain a better fit between the final exchange complex and pore water. Calcite and dolomite were assumed to dissolve and precipitate according to a kinetic law (Chou et al, 1989), and gypsum was assumed in equilibrium. Finally, the sulfate reduction at expenses of acetate was considered as a kinetic first order equation with respect to the acetate concentration.

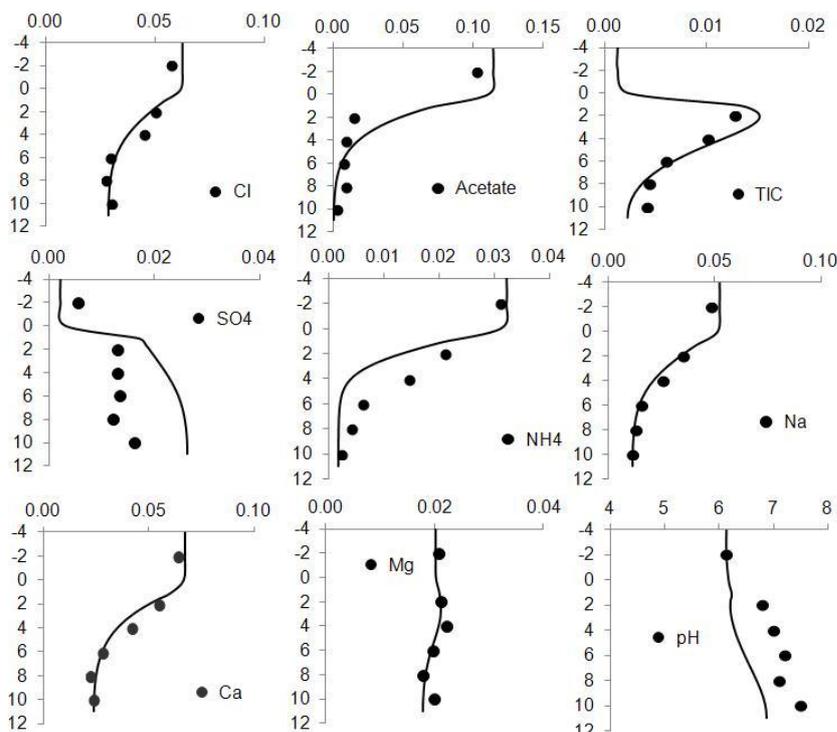


fig. 1. Pore water composition after the experiment: horizontal scale in mol/kgw, and vertical scale in cm (negative vaues correspond to supernatant leachate). Dots are experimental values and solid lines calculated.

palabras clave: Lixiviado acetogénico, Difusión, Intercambio catiónico, Sulfato-reducción, Transporte reactivo, Arcilla de Bailén

key words: Acetogenic leachate, Diffusion, Cation exchange, Sulfate-reduction, Reactive transport, Bailen clay

RESULTS AND DISCUSSION

The Cl final concentration in the clay porewater increases towards the leachate boundary showing a characteristic diffusion profile (Figure 1). A pore diffusion coefficient, D_p , (including tortuosity) of 10^{-10} m²/s was obtained fitting the Cl distribution and assuming that it is a conservative anion.

Diffusion of acetate from the supernatant causes the reduction of the SO₄ in the pore water. As SO₄ is reduced, the pore water becomes subsaturated with respect to gypsum and it dissolves fast to equilibrium (Figure 2). An increase in total inorganic carbon (TIC) also expected from the SO₄ reduction. This parameter is very sensitive to the reaction rate, and, therefore, the fitting of the experimental TIC values in the pore water allows to estimating a SO₄ reduction rate of 1.5×10^{-7} sec (half reaction time of 61 days).

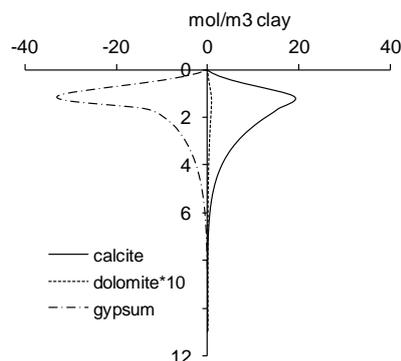


fig. 2. Calculated distribution of mineral dissolved (<0) and precipitated (>0) after 77 days of experiment.

The supernatant leachate is subsaturated in calcite and dolomite and diffusion of protons would cause the dissolution of both carbonates in the solid phase.

However, the increase in Ca, TIC and pH caused by SO₄ reduction and gypsum dissolution makes the pore water solution supersaturated with respect to calcite and dolomite and they precipitate (Figure 2). The predicted impact of solid phase changes in porosity after 77 days of experiment is minor. The observed pH values are higher than those calculated, probably due to the anomalously high pH caused by CO₂ loss of pressure during extracting pore water.

Diffusion of NH₄ and Na from the leachate into the clay is evidenced by the solute profile (Figure 1). Part of the diffused NH₄ and Na replaces Ca and Mg in the exchange complex as evidenced in the distribution of the exchange complex with depth (Figure 3). The exchange reactions cause an additional increase in Ca and Mg that is added to that of gypsum dissolution. The Mg plot in pore water shows this small increase, whereas the Ca increase is overprinted by gypsum dissolution and calcite precipitation. Due to the lack of gradient between the supernatant and the pore water, K concentration is only barely affected by diffusion.

SENSITIVITY OF THE MODEL

Once the model is calibrated with the experimental values, the results under in different scenarios can be tested. Thus, if gypsum is absent from the initial clay rock, acetate is less oxidized and much higher concentration of it reaches the bottom of the clay barrier earlier. The variation of the exchange complex composition is very minor. The presence or absence of carbonates in the initial clay rock does no modify the final results. This is of course expected since no carbonate dissolution takes place

along the experiment. If no CEC in the clays is assumed, the most relevant change is the NH₄ profile which is only controlled by diffusion, and reaches the bottom of the clay barrier with much higher concentration.

CONCLUSIONS

From the results obtained of this work, conservative anions, such as Cl⁻, show a characteristic diffusion profile. In contrast, the diffusion of the rest of the solutes into the clay triggers a set of reactions with the solid phase. Thus, desorption of Ca²⁺ and Mg²⁺ in the exchangeable complex occurs during the sorption of NH₄⁺ (mainly) and Na⁺ from the leachate. Diffusion of acetate causes the sulfate reduction, which induces the dissolution of gypsum, the supply of more Ca to the pore water and the calcite precipitation. Therefore, the presence of gypsum consumes acetate and delays its leakage through the clay liner. The dissolution of gypsum and precipitation of calcite do not cause significant changes in the final porosity of the clay.

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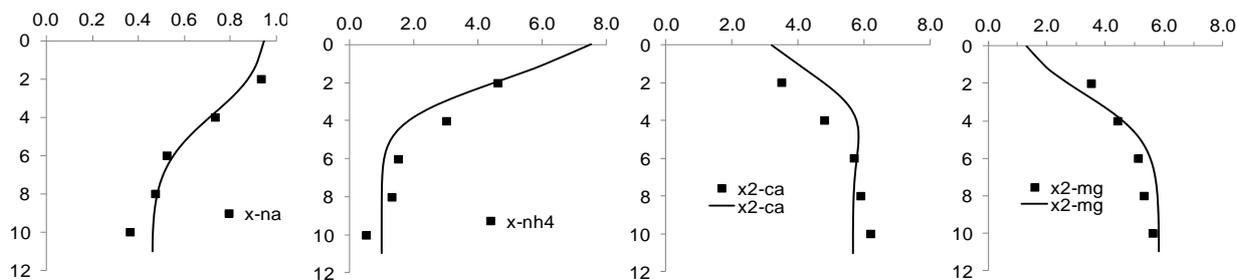


fig. 3. Composition of the Exchange complex after 77 days of the experiment: horizontal scale in cmol/kg solid, and vertical scale in cm. (negative values correspond to the supernatant leachate). Dots are experimental values and solid lines calculated.