



Improvement of attenuation functions of a clayey sandstone for landfill leachate containment by bentonite addition

Ana I. Ruiz ^{a,*}, Raúl Fernández ^a, Nicanor Sánchez Jiménez ^b, Manuel Rodríguez Rastrero ^a, Mercedes Regadío ^a, Isabel S. de Soto ^a, Jaime Cuevas ^a

^a Departamento de Geología y Geoquímica, Universidad Autónoma de Madrid, Facultad de Ciencias, Campus de Cantoblanco, 28049 Madrid, Spain

^b Departamento de Química Analítica y Análisis Instrumental, Universidad Autónoma de Madrid, Facultad de Ciencias, Campus de Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

Enhanced sand–clay mixtures have been prepared by using a sandstone arkosic material and have been evaluated for consideration as landfill liners. A lab-scale test was carried out under controlled conditions with different amended natural sandstones whereby leachate was passed through the compacted mixtures. The compacted samples consisted of siliceous sand (quartz–feldspar sand separated from the arkose sandstone) and clay (purified clay from arkose sandstone and two commercial bentonites) materials that were mixed in different proportions. The separation of mineral materials from a common and abundant natural source, for soil protection purposes, is proposed as an economic and environmentally efficient practice. The liner qualities were compared for their mineralogical, physicochemical and major ions transport and adsorption properties. Although all samples fulfilled hydraulic conductivity requirements, the addition of bentonite to arkose sandstone was determined to be an effective strategy to decrease the permeability of the soil and to improve the pollutants retention. The clay materials from arkose sandstone also contributed to pollutant retention by a significant improvement of the cation exchange capacity of the bulk material. However, the mixtures prepared with clay materials from the arkose, exhibited a slight increase of hydraulic conductivity. This effect has to be further evaluated.

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1. Introduction

Modern landfills are highly engineered containment systems that are designed to prevent or minimize the impact of solid waste on the environment and human health. Different barrier layers have been used as compacted soil liners for this purpose, including geosynthetic clay liners, capillary barriers and composite liners with geomembranes above compacted soil liners (Melchior, 1997).

Research into the containment functions of these barriers has been primarily based on favorable hydraulic performance. Many different natural materials have been considered for use as components in landfill liners, and these materials have been tested to evaluate their performances. Since the early 1950s, a great deal of effort has been put into studying the hydraulic conductivities of fine-grained soils (Lambe, 1954; Mitchell et al., 1965; Daniel, 1984). Among the materials studied, bentonite is often used and is usually coupled with other materials. In the 1980s, particularly in the Central European countries (Austria, Benelux, Germany and Switzerland), intensive research and qualification tests of natural sealing materials for municipal landfills were carried out. This led to the increase in popularity of sand–bentonite

mixtures, usually referred to as bentonite-enriched sand, or simply enhanced sand, for use in landfill liners because they can be engineered to possess the requisite low hydraulic conductivity and are less susceptible to frost damage or drying shrinkage compared to compacted clays (Abeele, 1986; Abichou et al., 2000; Bucher and Müller-Vonmoos, 1989; Chapuis, 1981; Chapuis, 1990; Czurda and Wagner, 1986; Garlanger et al., 1987; Gleason et al., 1997; Howell and Shackelford, 1997; Kenney et al., 1992; Krauss et al., 1997; Koch, 2002; Lundgren, 1981; Mollins et al., 1996; O'Sannick et al., 1995; Roehl and Czurda, 1997; Roehl and Czurda, 1998; Sällfors et al., 1986; Simons et al., 1987; Van Veen, 1983).

Subsequently, bentonite-enhanced sand mixtures have increasingly been used as landfill liners, the mixtures consisting of two different natural materials, granular soil and bentonite, well defined in terms of grain size, permeability, chemical activity and strength. These compacted mixtures are an economical alternative to the installation of a new engineered compacted clay liner, when suitable clay is not locally available. The base material, sand, is usually a local material and can differ from place to place. Very often, granular soils may contain a significant amount of clay. Therefore, these materials are expected to influence the engineering of sandy soils (Monkul and Ozden, 2007). Kenney (1997) postulated that the properties of these mixtures, which are composed of crushed quartz and different clay minerals, depend on the relative volume of the clay mineral matrix

* Corresponding author. Tel.: +34 91 497 30 47; fax: +34 91 497 49 00.

E-mail address: anai.ruiz@uam.es (A.I. Ruiz).

and should be useful as a clay hydraulic barrier under certain compacted conditions.

Kenney et al. (1992) reported the behavior of sand–bentonite mixtures with different ratios of these materials, and it was determined that the addition of relatively small amounts of sodium bentonite, approximately 5–10% of the dry weight of the sandy material, was suitable for proper liner function. When using calcium bentonite, the amount of granular material added should be doubled to provide low permeability and an enhanced, mechanically stable material (Iizuka et al., 2003). However, when greater amounts of bentonite are used, this highly plastic clay tends to form coatings around the sand grains, and the mixture becomes difficult to compact (Sällfors and Öberg-Högsta, 2002).

Attenuation of pollutants in clay–sand mixture landfills is mainly due to adsorption processes, which consist of the transfer of solutes from the liquid phase to the surface of the solid particles. The sorption of the many chemicals present in the leachate, such as ammonium, to bentonite is essentially an ionic exchange reaction. In landfill interior regions, anaerobic conditions typically prevail. Among the compounds present in municipal solid waste (MSW) landfill leachate, alkaline compounds, chloride and ammonium are present at high concentrations. The concentration of the ammonium cation remains constant even over long periods of time (i.e., 10 years) (Pivato and Raga, 2006). Therefore, due to its known toxicity and the fact that it is not degraded under anaerobic conditions, the ammonium cation is viewed as a key indicator of contamination caused by the leachate of a particular landfill (Clement et al., 1997; Pivato and Gaspari, 2006).

The aim of this study is focused on the natural attenuation of the migration of leachate contaminants composed of ammonium salts, either in amended natural soil or in sand–bentonite mixtures. For this study, arkose sandstone–bentonite compacted mixtures such as arkose purified sand–bentonite and arkose–bentonite were prepared and compared to evaluate their use as an isolation material in underground waste disposal. These specimens were prepared and tested for hydraulic conductivity in the laboratory under controlled conditions. Simulations of long-term diffusion transport and geochemical processes in an ideal landfill were also performed.

2. Materials and methods

2.1. Materials

The materials used in this investigation were two commercial bentonites and a granular material, a slightly plastic arenite (sandstone arkosic materials obtained from the Madrid Basin, Spain). The two selected bentonites were MX-80, an international reference of a natural Na-bentonite (Wyoming, USA), and Bentonil® C2, which is currently being used in Spain for civil engineering purposes and corresponds to a sodium-activated bentonite (commercialized by Süd-Chemie AG). The sand used was a quartz sand with a high proportion of feldspars that was separated from the arkose sandstone. The natural granular material, with a high proportion of fines (20% < 0.08 mm), was subjected to repeated dispersion and sedimentation processes to separate the fines and the quartz–feldspar sand (0.08–2 mm). The qualities of the different materials used in the experiments (sand, fines, MX-80 and Bentonil® C2 bentonite) were studied by assessing their mineralogy characterization by X-ray diffraction (XRD) and physicochemical properties, such as the external specific surface (BET-N₂), cationic exchange capacity (CEC) and the distribution of exchangeable cations (EC).

A synthetic landfill leachate was used in transport experiments. The leachate was composed of a simplified formulation of the landfill leachate obtained from El Garraf Landfill (Cuevas et al., 2009) and consisted of NH₄Cl (0.25 M), CH₃COONa (0.15 M) and NaHCO₃ (0.1 M), with a pH of 7.8. The composition and pH values were representative of an aged landfill in the methanogenic stage (Cuevas et al., 2011; Pivato and Raga, 2006; Williams, 1998). In addition, the leachate was

spiked with ions of the heavy metals (HM) Pb²⁺ and Cd²⁺ at concentrations of 100 µg/l to serve as tracers of HM migration.

2.2. Experimental design

Four sandstone–bentonite amended mixtures were prepared with sand, fines and bentonite powder in varying proportions, as presented in Table 1. These mixtures were uniformly mixed, poured and packed into a permeability cell. The compacted mixtures were prepared in a column of 3.5 cm in length and 5 cm in diameter and were packed at the standard Proctor dry density with a uniaxial press. The cell consisted of a Teflon cylinder (inner diameter: 5.0 cm) and an adjustable piston (Fig. 2a). The cell was confined in a stainless steel mold (Fig. 2b). The experiment was performed by forcing the leachate through the bottom of the cell with a constant injection pressure (600 kPa) by a piston pump. The effluent was collected from the upper part of the cell in a syringe collector.

Several hydraulic conductivity (HC) tests were performed previously on the sand–bentonite mixtures, and it was determined that the density of the compacted clay required for maintaining a low HC value is critical. In previous experiments, it was determined that in arenite–bentonite mixtures, the HC increases drastically at densities lower than 1.9 g cm⁻³ (Ruiz et al., 2009). For this reason, the compacted material was carefully weighed and packed to assure the achievement of the target proctor density (Table 1).

All columns were injected with distilled water (DW) prior to leachate percolation to achieve a constant flow rate and saturate the columns. As far as this flow rate was not controlled by changing injected or back pressure (not used), this flow is characteristic for the initial conditions of the performed experiments. This step also served to leach any soluble salts from the cell and allowed establishment of a baseline pore water chemistry for comparison with the leachate flow. This condition was maintained for approximately two months and was followed by pumping the synthetic leachate through the artificial mixture. The columns were flushed with leachate until the concentrations of inorganic solutes (Cl⁻, Na⁺ and NH₄⁺) in the effluent had attained apparent constant values. The effluent samples were collected after they reached volumes of 5–10 ml in the syringes. Finally, the cells were dismantled and the sand–clay columns were divided into three longitudinal sections. No significant differences were measured related to HM content, which lay within the experimental error of the determination techniques. Thus, data on chemistry within the solid is not presented.

2.3. Analytical methods

The mineralogical analysis of the samples was carried out by XRD analysis using a PANalytical X'Pert PRO diffractometer with Ge (111) as the primary monochromator. This procedure allowed for the selection of CuKα₁ radiation, which was analyzed with an X'Celerator detector. The samples were registered in the range of 3° < 2θ° < 70°, with a step size of 0.0167° and a counting time of 100 s for each step. The bulk sample was analyzed by the random powder method, and the oriented slides method was applied for the 2 µm and under size fraction, which was saturated in an Mg²⁺ solution (Moore and Reynolds, 1989). The XRD estimation for the content of the clay minerals in the

Table 1
Proportions of sand, fines and bentonite used in samples tested.

Samples	Sand (without fines) (%)	Fines (%)	MX-80 (%)	C2 (%)	Dry density (g·cm ⁻¹)
80s20f (a)	80	20	–	–	2.07
88s10f + 2MX-80 (b)	88	10	2	–	2.07
95 s + 5MX-80 (c)	95	–	5	–	1.95
95 s + 5 C2 (d)	95	–	–	5	2.00

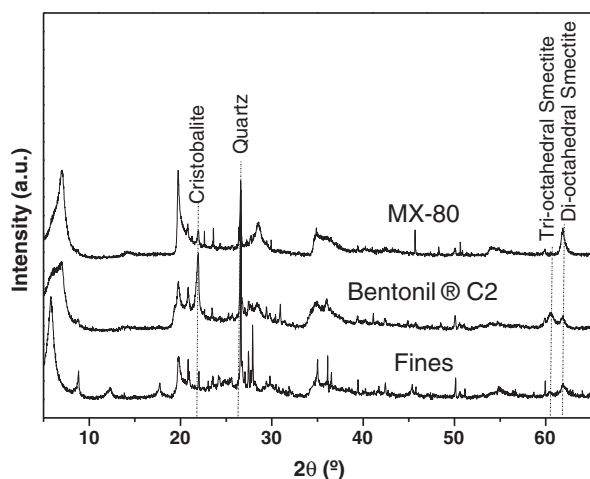
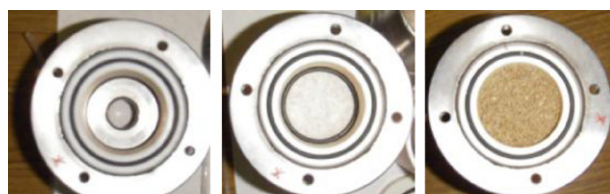


Fig. 1. X-ray diffraction patterns for two commercial bentonites (MX-80 and Bentonil® C2).

clay fraction, mainly illite (10 Å), kaolinite, chlorite (7.1 Å) and smectite (18 Å under glycerol solvation), was performed as previously described by Barahona (1974).

The specific surface area was determined by BET analysis (multi-point N_2 adsorption, micromeritics® GEMINI V after degassing under



a



b

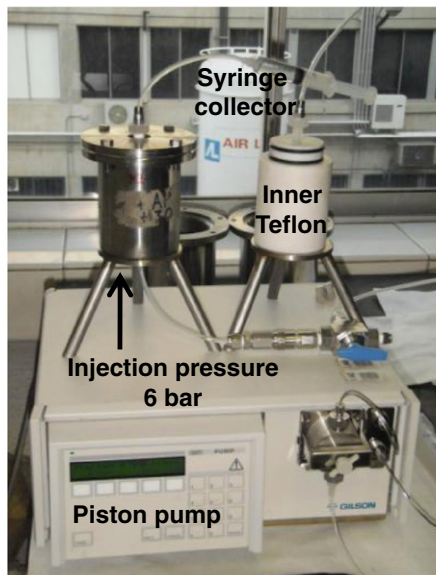


Fig. 2. (a) The sequence of filling the transport cells with the compacted material. (b) Experimental device.

N_2 flow for 18 h at 90 °C (UNE 22-164/94)). For the surface chemistry analysis, exchangeable NH_4^+ were extracted from the clay at room temperature (Thomas, 1982), and analyzed using ion-selective potentiometry (ORION® 9512 Ammonia Gas-Sensing Electrode). The (CEC) of the original clay was determined at room temperature by Na^+ homoionization (1 M $NaCOOCH_3$ at pH 8) and Mg^{2+} displacement (0.5 M $MgNO_3 \cdot 5H_2O$ at pH 5) (Rhoades, 1982).

NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Cl^- ions were analyzed by ion chromatography using a Metrohm™ 882 Compact IC plus in the collected liquid samples. Cadmium and Pb analyses in the collected liquid samples were carried out by Atomic Absorption Spectrometry (AAS) with graphite furnace atomization. To determine the HM ions content in the clay samples, the samples were dried and digested in a microwave oven (Perkin-Elmer Anton-Paar Microwave Sample Preparation System model Multiware) in aqua regia for 30 min. After the sample was cooled, the digests were filtered and diluted with ultrapure water. The metal concentrations in these solutions, from liquid and solid samples, were measured by AAS using a Solaar M series Unicam Atomic Absorption Spectrophotometer with the experimental conditions recommended by the manufacturer.

2.4. Reactive transport modeling

The reactive transport geochemical model, CrunchFlow (Steeffel, 2006), was used to simulate the advective column experiments. The system consisted of a unidimensional column divided into several homogeneous cells and consisting of clay minerals (with CEC), quartz, calcite and chloride-dominant pore water. A constant synthetic solution that simulated the aqueous leachate was located in a ghost cell out of the domain, adjacent to the first cell, and was percolated through the column, which reacted with the minerals and fluids in each cell by user-defined kinetic rate laws and thermodynamic equilibrium. The main contribution of the model was the capability to reproduce the reactivity observed in the experiment using the transport of aqueous species, pH buffering and exchange reactions. Only experiments with higher and lower HC were modeled (samples 80s20f and 95 s + 5 C2).

3. Results and discussion

3.1. Characterization – XRD, BET- N_2 , CEC and EC

The mineral compositions of the two commercially available bentonites that were studied were determined by XRD analysis and are shown in Table 2 and Fig. 1. The XRD patterns indicated that the main components were minerals of the smectite group, and a substantial amount of quartz impurities was observed in the bulk material in addition to minor amounts of Na and K feldspars, calcite and dolomite.

Significant amounts of cristobalite were found in Bentonil® C2 and a strong (060) reflection at d approx. 1.53 Å suggested the trioctahedral nature of smectite. However, MX-80 bentonite, with a (060) spacing at 1.50–1.51 Å, indicated that the clay mineral predominantly consisted of a dioctahedral smectite. Additional data provided by the commercial companies did not mention the presence of any special additive, i.e. polymers, which is confirmed by a weight loss of <6% on calcination.

The clay mineralogy of fines from the arkose sample was dominated by dioctahedral smectite with some kaolinite and illite and accessory minerals such as quartz, K and Na feldspars. The primary component of the sandy material (without fines) was quartz, which was accompanied by feldspars.

The characterization of the surface-chemical properties of the bentonites revealed a predominance of Na^+ on exchangeable sites and a high cation exchange capacity. The Bentonil® C2 bentonite was prepared commercially as a fine powder in contrast with the granular appearance of MX-80. Bearing this in mind, MX-80 was

Table 2
Mineralogical semi-quantification (wt.%) and physical–chemical parameters of the materials.

Materials	Sheet-silicates				Qtz	Pl	Kfs	Cal	Dol	BET-N ₂ (m ² ·g ⁻¹)	CEC (cmol(+)/kg)	Interlayer cations
	T	Kln	Ill	Smt								
Sand	7	–	2	5	62	10	21	–	–			
Fines	86	15	14	70	5	2	3	–	–	53	61	Ca, Mg
MX-80	88	–	–	88	12	<1	<1	<1	<1	54	91	Na (Ca/Mg)
C2	73	–	5	68	24	<1	1	1	1	95	63	Na

T: Total amount of clay minerals; Kln: Kaolinite; Ill: Illite; Smt: Smectite; Qtz: Quartz; Pl: Plagioclase; Kfs: K-feldspar; Cal: Calcite; Dol: Dolomite.

grinded to a micron size powder with a Zircon microball mill RETSCH™ MM200. Independently of the grinding size, the high specific surface corresponds to Bentonil® C2 bentonite, whereas the CEC was higher for MX-80 bentonite (Table 2).

3.2. Hydraulic conductivity

When the synthetic leachate was pumped through the artificial mixtures, a disturbance in the DW stabilized HC was observed (Fig. 3), with the sand and MX-80 bentonite ± arkosic fines mixtures presenting the highest disruption. By contrast, the experiment that corresponded to the mixture of sand and Bentonil® C2 displayed the lowest HC and only a minor disturbance during leachate pumping. This finding is illustrated in Table 3 by the small difference between the HC values with DW and the measurements after leachate infiltration.

Fig. 4 shows that all four samples have low HC values ($<1 \cdot 10^{-9} \text{ m} \cdot \text{s}^{-1}$), which fulfill the technical requirements for landfills that contain municipal waste (1999/31/EC, 1999) either before or after leachate infiltration. The artificial arkose sample (sand + fines) had the highest HC value, and it was not disrupted by the injected leachate. The HC increased, in response to leachate infiltration, by as much as one order of magnitude. The high specific

surface value of Bentonil® C2 bentonite compared to MX-80 could be responsible for the remarkable resistance to changes in hydraulic properties in the Bentonil® C2 mixture.

3.3. Effluent composition

The collected effluent compositions at different pore volumes were used to compare the behaviors of chloride, cations (Na^+ , K^+ , NH_4^+ , Mg^{2+} and Ca^{2+}), pH and HM ions during leachate infiltration. The breakthrough curves for inorganic solutes are presented in terms of dimensionless normalized solute concentration (C/C_0) against pore volume of fluid eluted through the column. Effluent concentrations of solutes are normalized to concentrations (C_0) in the leachate. The breakthrough curve ends where the concentration of effluent equals the concentration of influent and has a value of 1, values $C/C_0 < 1$ indicate mass loss from solution and mass uptaken by compacted probe. Fig. 5 shows the differences in ionic transport between the arkosic sample and the bentonite mixtures in relation to variations in pH.

The bentonite mixtures needed smaller pore volumes to reach a constant regime close to $C/C_0 = 1$ of the Na^+ and NH_4^+ concentrations compared to the arkosic mixtures. This fact is related to the total CEC supplemented by the smectite-rich content of the arkosic

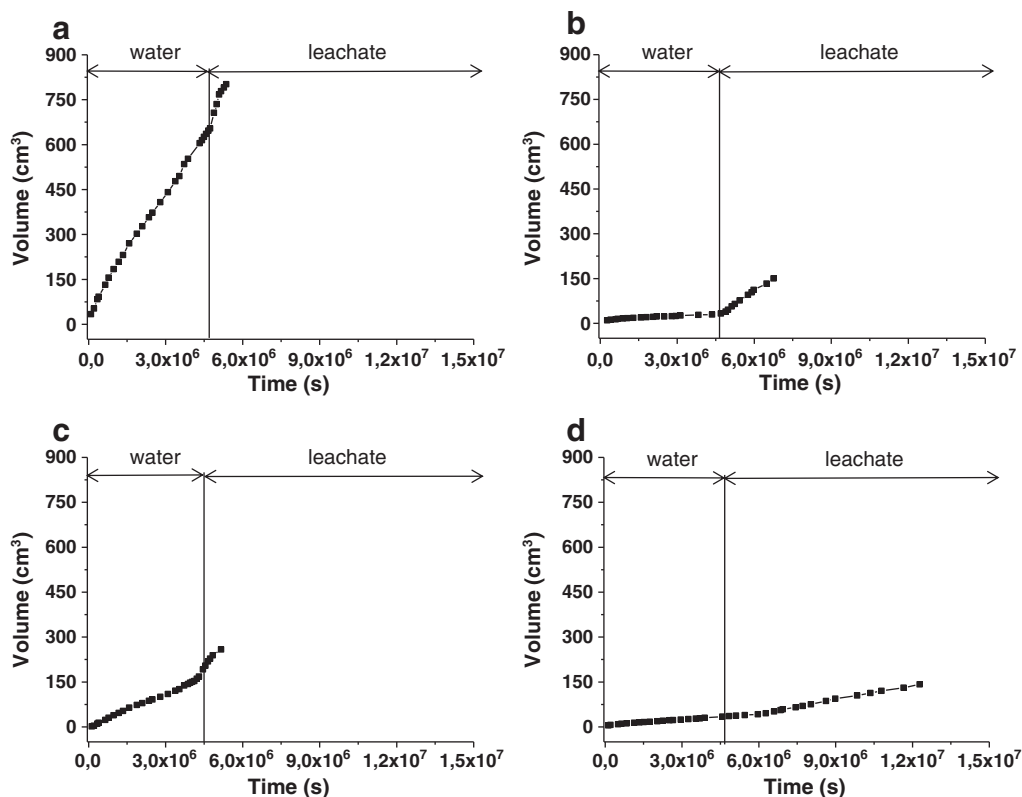


Fig. 3. Transport experiment: volume vs. time: (a) 80s20f, (b) 88s10f + 2MX-80, (c) 95 s + 5MX-80 and (d) 95 s + C2, as listed in Table 1.

Table 3

Hydraulic conductivity values before (HC_0) and after (HC_L) to pump leachate and the maximum value reached of HC_L (HC_L max) and threshold pore volume for the breakthrough of the dissolved ions in dissolution; cationic exchange capacity and exchanged ammonium at the end of the experiments in the arenite–sand–bentonite mixtures.

Samples	HC_0 ($m \cdot s^{-1}$)	HC_L ($m \cdot s^{-1}$)	HC_L max ($m \cdot s^{-1}$)	Pore volume			CEC ($cmol(+)/kg$)	NH_4^+ exchange ($cmol(+)/kg$)
				Cl^-	Na^+	NH_4^+		
80s20f	$4 \cdot 10^{-11} \pm 1 \cdot 10^{-11}$	$5 \cdot 10^{-11} \pm 3 \cdot 10^{-11}$	$1 \cdot 10^{-10}$	2.0	7.0	12.0	12.1	10.2 ± 0.1
88s10f + 2MX-80	$1 \cdot 10^{-12} \pm 7 \cdot 10^{-13}$	$2 \cdot 10^{-11} \pm 5 \cdot 10^{-12}$	$3 \cdot 10^{-11}$	2.5	>4.5	>4.5	7.9	7.4 ± 1.0
95 s + 5MX-80	$1 \cdot 10^{-11} \pm 3 \cdot 10^{-12}$	$3 \cdot 10^{-11} \pm 1 \cdot 10^{-11}$	$5 \cdot 10^{-11}$	3.0	4.5	4.5	4.6	5.8 ± 0.6
95 s + 5 C2	$2 \cdot 10^{-12} \pm 7 \cdot 10^{-13}$	$5 \cdot 10^{-12} \pm 1 \cdot 10^{-12}$	$9 \cdot 10^{-12}$	>3.0	>3.0	>3.0	3.2	4.0 ± 0.4

finer (Table 3). The absolute amount of ammonium retained relative to the number of pore volumes was proportional to the total exchange capacity of the mixture. Retardation of Na^+ and NH_4^+ fronts is observed being the NH_4^+ cation clearly more selective than Na^+ . The original Ca^{2+} and Mg^{2+} sorbed cations in the arkosic fines result desorbed from the host substrate by the injection of the leachate with a high proportion of Na^+ and NH_4^+ (Fig. 6a and b). The addition of sodium bentonites to the pure sand material also enabled the mixture the ability to release divalent cations (Ca^{2+} and Mg^{2+}), but in minor quantities, probably due to the dissolution of carbonate traces present in both bentonites (Fig. 6c and d). This finding suggests that leachate impact in the barrier properties of commercial sodium bentonites/sand mixtures is less important compared to the natural smectite (divalent exchanged) present in the tested natural soil.

With regard to the variation in pH of the effluent pore volume, when NH_4^+ was retained, the effluent pH decreased and then increased with the exit of this cation as its concentration approached $C/C_0 \approx 1$.

With respect to the anionic transport, the anion exclusion effect considers that the volume available for anions to move through a montmorillonite-rich clay is smaller than the total pore volume due to the influence of the diffuse double layer adjacent to the negatively charged clay surfaces from which anions are excluded (Appelo and Wersin, 2007; Bradbury and Baeyens, 2003; Muurinen et al., 2007; Wersin et al., 2004). In these experiments, the number of pore volumes required for chloride to approach $C/C_0 = 1$ increased apparently according to the decrease in the CEC. The decrease of CEC, in fact, is related to the use of just small amounts of Na-bentonite, without the addition of the high CEC smectitic arkosic fines. In the case of Bentonil® C2, with the lowest CEC, the magnitude of its external specific surface seems to enhance anion exclusion.

Fig. 5 shows the mobility of chloride, which indicates an apparent anion retention because the number of pore volumes at chloride $C/C_0 = 0.5$ is <1 in the arkosic sample and 1.1, 1.4 and 1.5 for the 2% MX-80, 5% MX-80 and C2 samples, respectively. Charlet and Tournassat (2005) found evidence of ion pairs sorption ($Ca-Cl^+$ and $Mg-Cl^+$) on

highly compacted montmorillonite to explain the behavior of semi-permeable membranes with anions when using sodium bentonites (Horseman et al., 1996; Kang and Shakleford, 2010; Malusis and Shakleford, 2002). In our case this effect cannot be taken into account because the leachate does not contain divalent cations. Moreover, the Ca–Mg smectite case (80s20f mixture) did not have significant chloride retention effects.

The initial concentrations of Pb^{2+} and Cd^{2+} species in the permeated synthetic leachate were sufficiently low and allowed for the presence of these metals as soluble species. The measurement of these components in the three analyzed solid sections fell within the experimental error of the determination techniques. However, these metals were present in the effluent (Fig. 7). Their concentration was <0.02 C/C_0 in six to seven pore volumes in the four experiments, demonstrating the high retention ability of low concentrations of soluble Pb^{2+} and Cd^{2+} species in a typical mature leachate. The retention process (ion exchange) is responsible for the retention of HM ions at >95% of their initial concentrations. However, the relative increase in concentration of HM ions in the effluent is related to the increase in HC values for the clay–sand mixtures. Therefore, the transport of HM ions is also limited by the effluent migration rate. Bentonil® C2 bentonite retains Pb^{2+} significantly less than Cd^{2+} .

3.4. Geochemical models

The model of the experiment performed with the arkosic sample (80s20f in Table 3) was characterized by the rapid transport of leachate through the column and was dominated by advection. The linear Darcy velocity used in the model ($3 \cdot 10^{-7}$ m/s) was based on determinations made under the hydraulic gradient imposed in the experiments. However, the diffusion coefficient at 25 °C (D_{25}) was arbitrarily assigned to $1 \cdot 10^{-10}$ m²/s. This D_{25} value lies within the range applied in similar column experiments at room temperature (see Fernández et al., 2009), who applied a slightly lower D_{25} value for compacted bentonite. The total porosity, which was assumed to

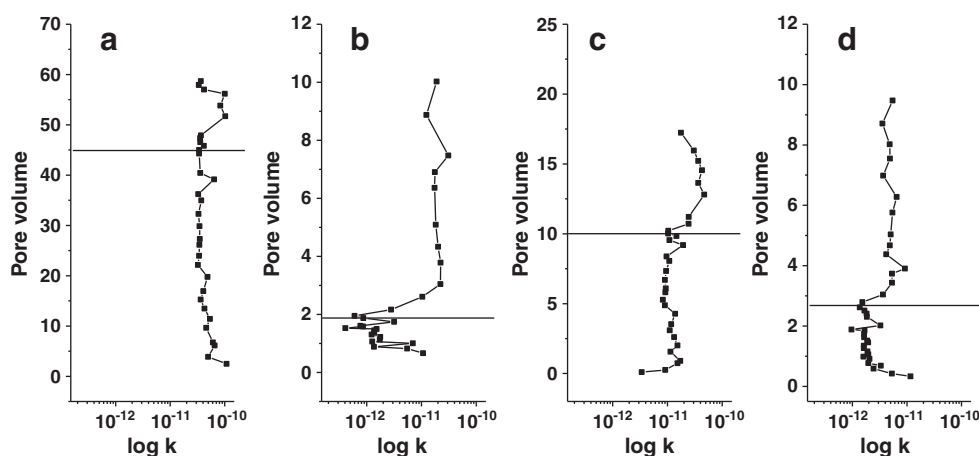


Fig. 4. Transport experiment: pore volume vs. hydraulic conductivity: (a) 80s20f, (b) 88s10f + 2MX-80, (c) 95 s + 5MX-80 and (d) 95 s + 5 C2, as listed in Table 1.

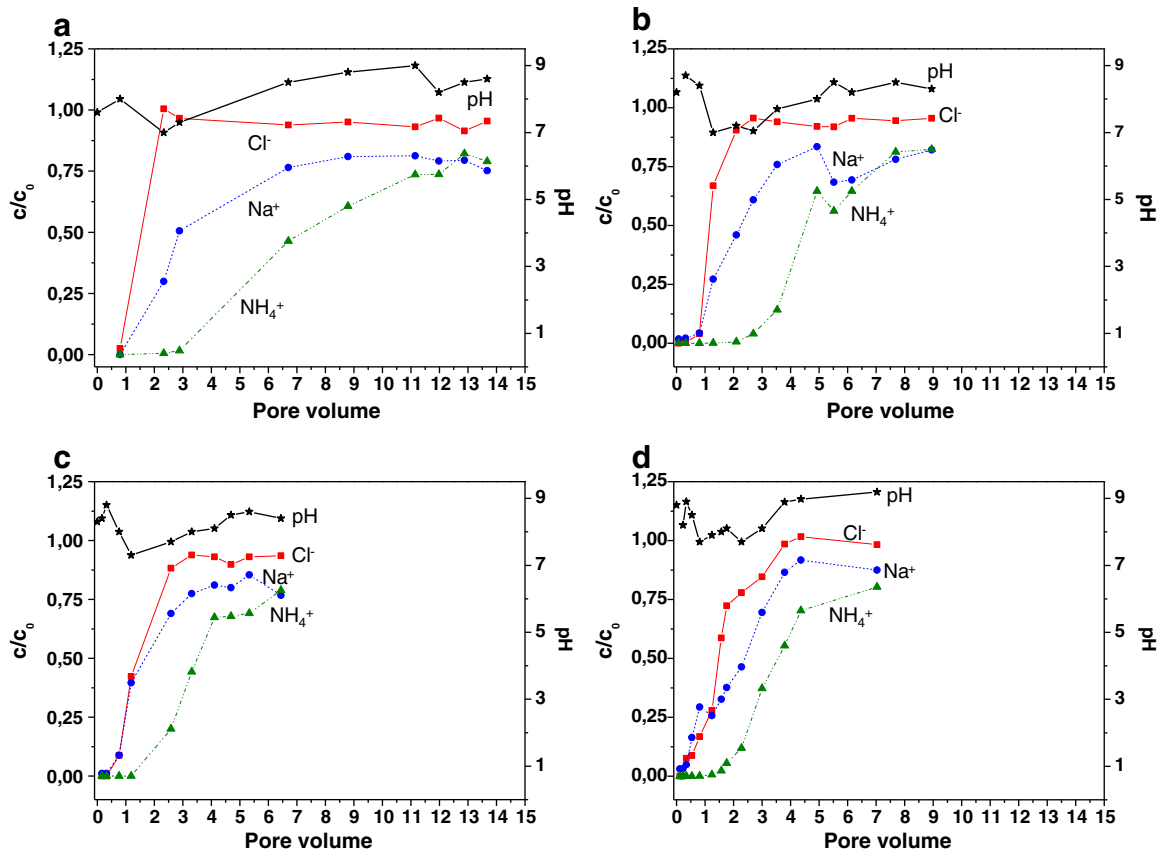


Fig. 5. Transport experiment: C/C_0 relative concentration of the major ions and pH vs. Pore volume: (a) 80s20f, (b) 88s10f+2MX-80, (c) 95 s + 5MX-80 and (d) 95 s + 5 C2, as listed in Table 1.

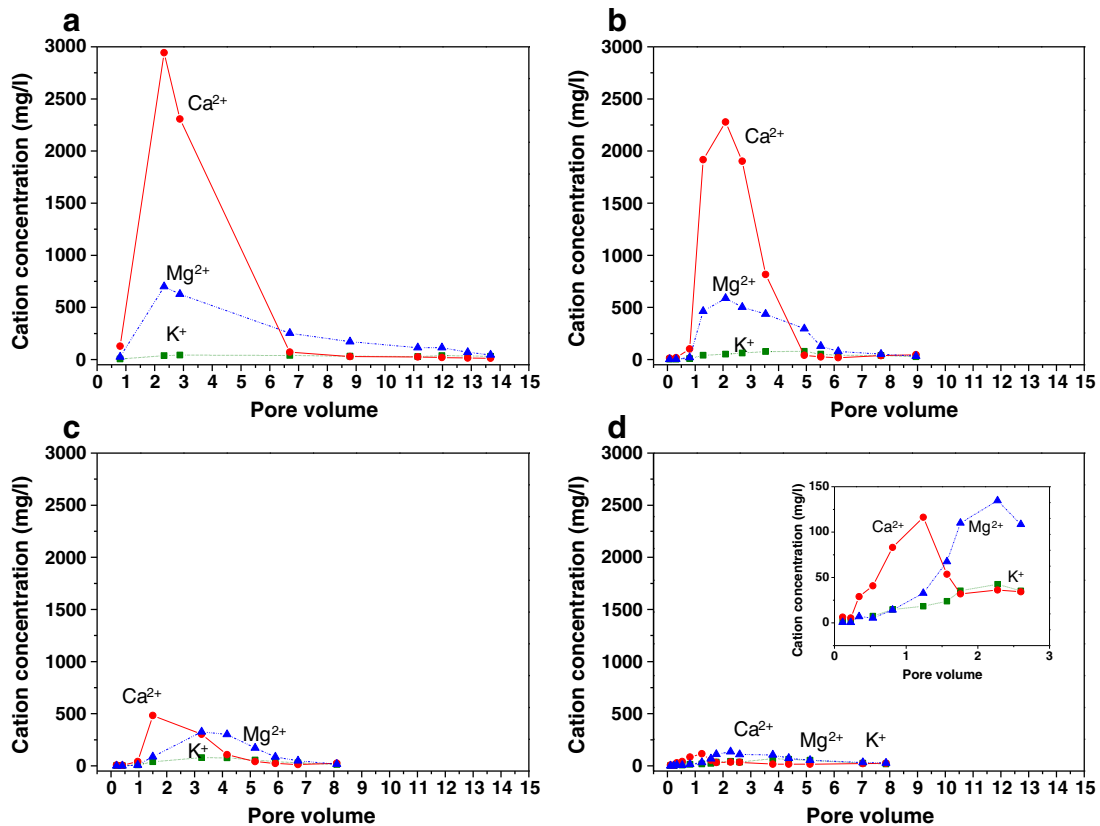


Fig. 6. Transport experiment: K^+ , Ca^{2+} and Mg^{2+} effluent concentration vs. pore volume: (a) 80s20f, (b) 88s10f+2MX-80, (c) 95 s + 5MX-80 and (d) 95 s + 5 C2, as listed in Table 1.

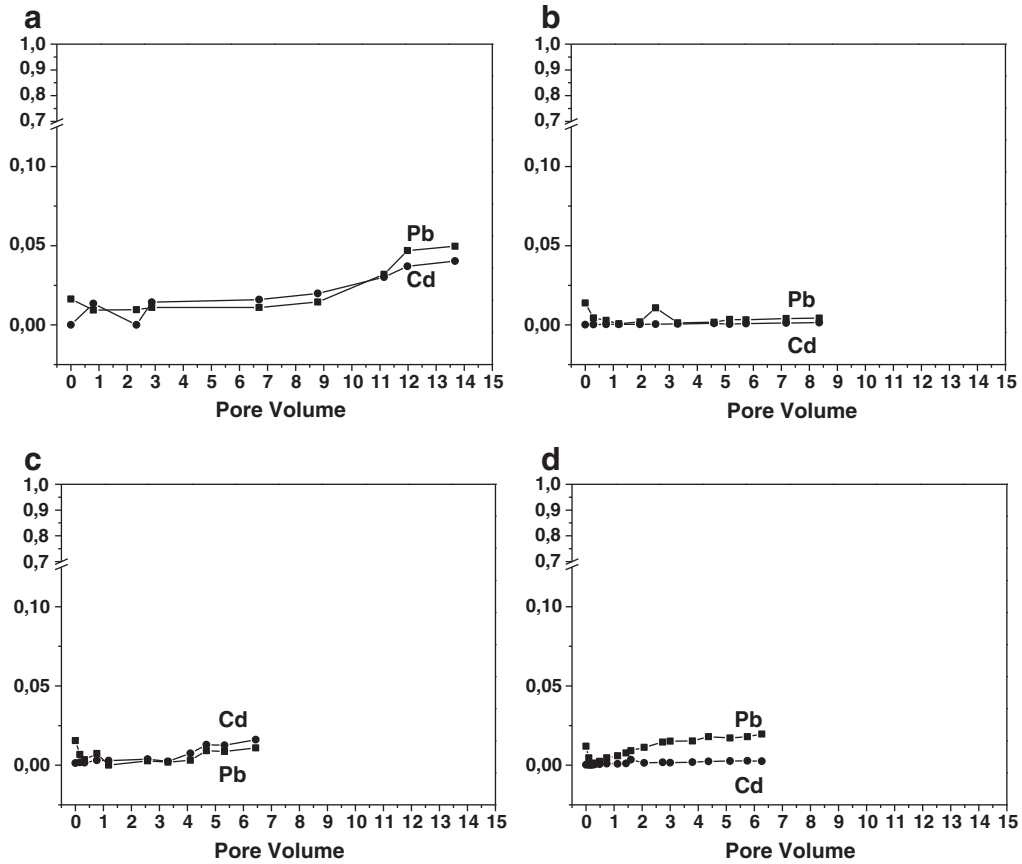


Fig. 7. Transport experiment: heavy metal (Pb and Cd) concentrations vs. pore volume: (a) 80s20f, (b) 88s10f+2MX-80, (c) 95s+5MX-80 and (d) 95s+5C2, as listed in Table 1.

be fully saturated, was calculated based on the experimental pore volume (20%), and the CEC was set to 12.1 cmol(+)/kg, with Ca^{2+} set as the dominant exchangeable cation. The model was run for 11 days to directly compare the experimental and modeled results.

The Darcy velocity used in the model of the experiment performed with the Bentonil® C2 sample (95c+5C2 in Table 3) was approximately one order of magnitude lower ($2 \cdot 10^{-8}$ m/s) than with sample 80s20f, but the D_{25} was considered to be unchanged. The CEC in this experiment was set to 3.2 cmol(+)/kg, with Na^{+} set as the dominant exchangeable cation. The porosity calculated in this experiment was 22%, and the model was run for 40 days.

The modeled pHs reproduced observed trends at the outflow for both experiments (Fig. 8). For the arkosic sample, a rapid decrease

in pH was predicted from a value near 8 to a value near 7 in the initial period. The pH increased slowly by approximately 0.5 units in 11 days. A similar trend (initial decrease and subsequent slow increase in pH) was determined experimentally, although the pH values were higher than in the predicted model, and some delay was observed in the experimental results when they were directly compared with the model. For Bentonil® C2 sample, a different behavior was observed with regard to pH. An increase from 7.5 to 9, followed by a decrease to 7.5, was predicted within the first five days of the reaction. The pH then increased slowly by approximately 0.5 units in 35 days. The initial increase and decrease in pH were determined by laboratory measurements but with a temporal delay. The time shift observed between the experimental and modeled results can be explained by the fact that the pH determined experimentally was measured in the effluent, while the model predicted pH values in the pore water of the last cell within the column.

The concentrations of ions in the effluents were influenced by linear advective velocities and cation exchange processes. The models satisfactorily reproduced the experimental concentrations of Na^{+} , Cl^{-} and NH_4^{+} in the effluent for both experiments (Figs. 9 and 10). For the arkosic sample, aqueous Cl^{-} quickly percolated through the column. Na^{+} was partially retained in the exchangeable region, and NH_4^{+} was extensively retained, displacing exchangeable Ca^{2+} . This ion equilibrium reaction produced a slower release of Na^{+} and NH_4^{+} ions in the effluent, as observed experimentally. For Bentonil® C2 sample, the release of Na^{+} was fast and comparable to that of Cl^{-} , due to the dominant Na^{+} concentration in the exchangeable region. NH_4^{+} in this experiment displaced the initial Na^{+} ions in the exchangeable region and therefore decreased the Na^{+} concentration in the effluent after 20–25 days.

Once the experimental results by the models in the two column experiments were validated, long-term models were performed for

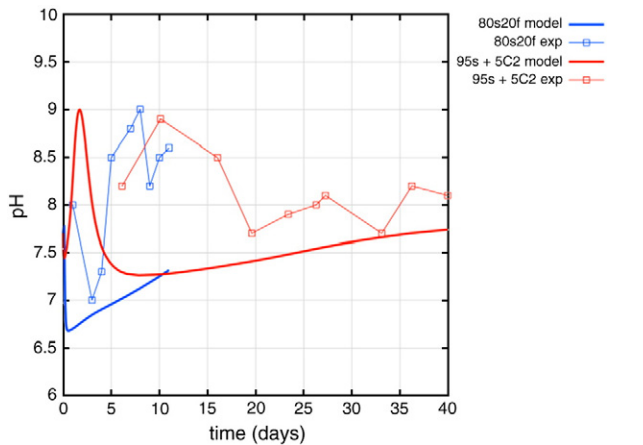


Fig. 8. Comparison of experimental and modeled pH for samples 80s20f and 95c+5C2.

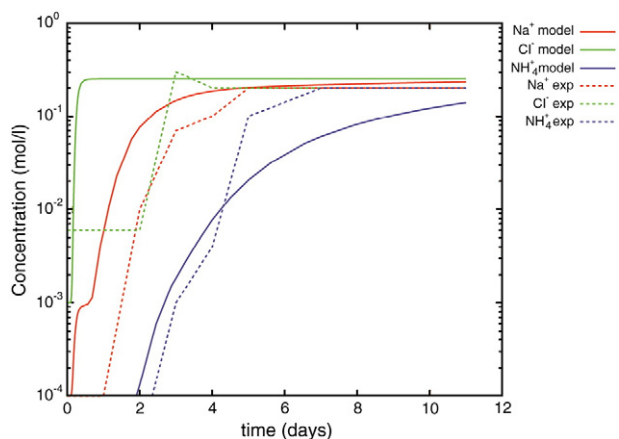


Fig. 9. Comparison of aqueous Cl^- , Na^+ and NH_4^+ determined experimentally in the effluent and modeled in the last cell of the column for sample 80s20f.

both cases to simulate the leaching behaviors of Cl^- , Na^+ and NH_4^+ as a function of time for up to 20 years, a typical life span of an active landfill. The chemical and mineralogical conditions were maintained as in the previous models; however, the physical dimensions of the columns were scaled to a thickness of 1 m, and advective transport was omitted. The linear velocities were matched to the HC calculated in each experiment, $5.06 \cdot 10^{-11}$ m/s (arkose) and $3.02 \cdot 10^{-12}$ m/s (Bentonil® C2 sand mixture), setting the hydraulic gradient to 1, with diffusion being the dominant transport mechanism.

The Na^+ or NH_4^+ -chloride plumes were not observed at a depth of 1 m in either case during the first 10 years (Fig. 11). However, after 10 years, the concentration of Cl^- that was released in the effluent was greater for the arkose than for the Bentonil® C2 sand mixture. Aqueous NH_4^+ was retained in the exchangeable region, and insignificant concentrations (on the order of 10^{-14} and 10^{-15} mol/l for both samples) were released to the effluent after 20 years in both models. These data establish soil-bentonite barriers as efficient materials during the typical lifetime of landfills.

4. Conclusions

This study has assessed the chemical impact of methanogenic leachate migration from landfills in laboratory column experiments and reactive transport modeling of the experimental data.

This study has demonstrated that ammonium chloride leachate produces a significant perturbation in the flow rate through the natural clay mixtures, and this effect is more pronounced when MX-80

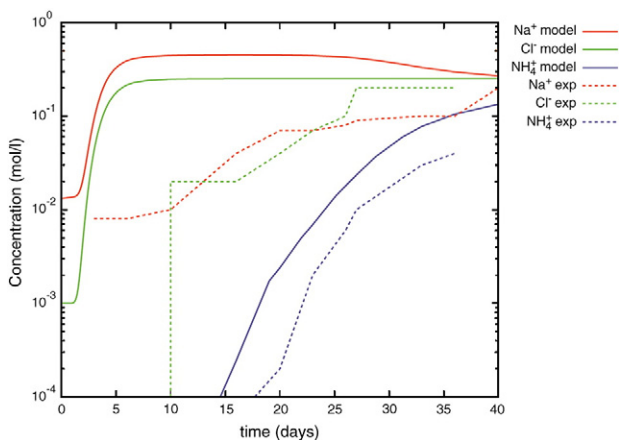


Fig. 10. Comparison of aqueous Cl^- , Na^+ and NH_4^+ determined experimentally in the effluent and modeled in the last cell of the column for sample 95c + 5 C2.

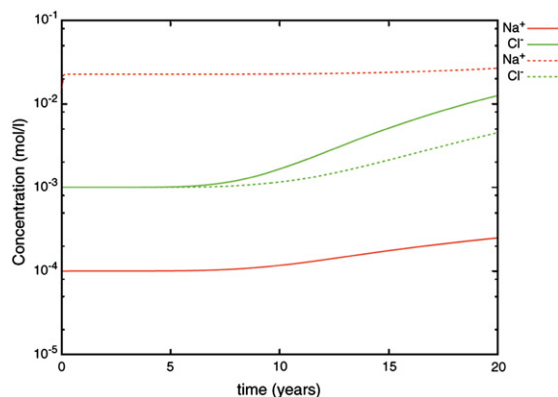


Fig. 11. Long-term evolution of aqueous Cl^- and Na^+ concentrations at the end of the column for sample 80s20f (solid lines) and sample 95c + 5 C2 (dashed lines).

is used in the mixture. Hydraulic conductivity increases as much as one order of magnitude, being inside the standard requirements ($\text{HC} < 10^{-10}$ m/s). The higher specific surface or the tri-octahedral character of Bentonil® C2 may have a role in minimizing the effect of this leachate when this bentonite is used. NH_4^+ is selectively retained compared to sodium and there is an almost complete substitution of the original exchangeable cations by the leachate cations. The amount retained, in terms of number of pore-volumes, is proportional to the total exchange capacity of the mixture. Chloride anions seem to be retained in the mixtures with bentonite and this process is probably due to the semi permeable behavior that bentonite confers to the mixture in highly compacted conditions. The effluent pH decreases when NH_4^+ is completely retained in the clay and pH increases when ammonium starts to flow with the effluent. The buffer capacity of the mixtures with bentonite is stronger than the arkosic material.

This experiment confirms that the soil-bentonite barriers are efficient to pollutant attenuation during the typical lifetime of landfills. On the other hand, clay materials in natural soils also contribute to the retention of pollutants and even to accomplish with regulations if they are properly compacted. However, the mixtures prepared with clay materials from the arkose, exhibited a slight increase of hydraulic conductivity. This effect has to be further evaluated.

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