

## A clay permeable reactive barrier to remove Cs-137 from groundwater: Column experiments



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### ABSTRACT

Clay minerals are reputed sorbents for Cs-137 and can be used as a low-permeability material to prevent groundwater flow. Therefore, clay barriers are employed to seal Cs-137 polluted areas and nuclear waste repositories. This work is motivated by cases where groundwater flow cannot be impeded. A permeable and reactive barrier to retain Cs-137 was tested. The trapping mechanism is based on the sorption of cesium on illite-containing clay. The permeability of the reactive material is provided by mixing clay on a matrix of wood shavings. Column tests combined with reactive transport modeling were performed to check both reactivity and permeability. Hydraulic conductivity of the mixture ( $10^{-4}$  m/s) was sufficient to ensure an adequate hydraulic performance of an eventual barrier excavated in most aquifers. A number of column experiments confirmed Cs retention under different flow rates and inflow solutions. A 1D reactive transport model based on a cation-exchange mechanism was built. It was calibrated with batch experiments for high concentrations of  $\text{NH}_4^+$  and  $\text{K}^+$  (the main competitors of Cs in the exchange positions). The model predicted satisfactorily the results of the column experiments. Once validated, it was used to investigate the performance and duration of a 2 m thick barrier under different scenarios (flow, clay content, Cs-137 and K concentration).

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### 1. Introduction

Cesium-137 (Cs-137) is one of the most common products of the nuclear fission of U-235 and Pu-239. Its high solubility and similarity to K facilitates its assimilation by living organisms, which makes it toxic and has motivated extensive studies on the environmental behavior of Cs-137. High Level Radioactive Waste (HLRW) repositories provide permanent insulation, but Cs is sometimes released to the environment due to leakage of nuclear installations (Smoot et al., 2011; Lichtenstein, 2004; Bea et al., 2004) or accidents like Chernobyl (The Chernobyl forum, 2005) and Fukushima (Yasunari et al., 2011).

Migration of Cs can be retarded by adsorption onto different materials. Disposal of HLRW is usually based on a multibarrier system to prevent leakage of these radionuclides to the environment. Clays are usually preferred for this purpose and are used as sealers in these repositories because of their low permeability and high sorption capacity. Thus, a number of authors have studied the

sorption of Cs on clays (Sawhney, 1972; Francis and Brinkley, 1976; Eberl, 1980) and, more specifically, on illite (Brouwer et al., 1983; Comans et al., 1991; Comans and Hockley, 1992; Cornell, 1993). Recently, sorption of Cs on different clay rocks has also been studied in batch experiments by Poinssot et al. (1999), Zachara et al. (2002) and Liu et al. (2003). All these studies concluded that illite is most responsible for cesium sorption, and Bradbury and Baeyens (2000) proposed a generalized cation exchange sorption model for the uptake of Cs by illite on the basis of mechanistic processes. According to this model, Cs sorbs onto illite by cation exchange at three sites with different affinity and capacity: FES (Frayed Edge Sites), type II and planar sites. The FES have the strongest affinity for Cs but the lowest capacity, and they are most effective at low concentrations ( $<10^{-7}$  M), where sorption is linear. Type II sites mainly contribute to sorption between  $10^{-7}$  M and  $10^{-4}$  M concentrations with a non-linear behavior. Sorption at planar sites is relevant at higher concentrations ( $>10^{-3}$  M) but can be considered negligible for low Cs concentrations (Bradbury and Baeyens, 2000).

The high sorption capacity of clay, together with its low-permeability, has prompted its use to prevent groundwater flow and seal the polluted area for different contaminants and

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specifically for Cs-137 (Krumhansl et al., 2001). However, there are cases where groundwater flow cannot be impeded. The present study is motivated by one such case at a real site in SW Spain. Material contaminated with Cs-137 was accidentally dumped, in 1998, at a surface repository of building and industrial waste confined by clay walls. The initial cleaning and restoration proved insufficient since some Cs-137 radioactivity leaked through fractures of the confining walls. Given that the repository is exposed to rain recharge and groundwater flow and discharge, it is not possible to intercept the groundwater with an isolation barrier. After the hydrogeological characterization of the repository, a Permeable Reactive Barrier (PRB) was proposed as the most adequate remediation option.

A Permeable Reactive Barrier (PRB) is an in situ remediation method for groundwater that retains the contaminant to prevent its migration downstream. The barrier involves digging a trench and filling it up with an adequate material (USEPA, 1998). This treatment requires the materials to be: 1) reactive, to trap or degrade the species of interest; 2) permeable, to allow water to flow through them; 3) passive, to work naturally with little maintenance and 4) inexpensive and accessible because of the large amount of filling material needed.

To meet the conditions required for the PRB filling material, we propose a powdered clay rock mixed with pine wood shavings. Similar mixtures with calcium carbonate or caustic magnesia instead of clay have resulted in very satisfactory hydraulic performance for one year both in laboratory columns and at field scale for mine drainage treatments (Rötting et al., 2008a,b,c; Caraballo et al., 2010, 2011a,b). Here we test the reactivity and permeability of this mixture by means of laboratory batch and column tests combined with reactive transport modeling. The aim of this study was to confirm the suitability of this mixture as an effective and economic filling material for a PRB to treat Cs-137.

## 2. Materials and methods

### 2.1. Material selection and characterization

The PRB filling material is a mixture of powdered clay rock and pine wood shavings. The latter are curved flakes of up to 2 cm length and about 0.5 mm thick. They are a waste from a furniture factory. Illite-containing clays from a local ceramics quarry were selected as a suitable reactive material because of their high illite content, and their availability and low cost. The average mineralogical characterization of the clay (in wt%) is: illite (57), quartz (27), dolomite (8), hematite (5), kaolinite (1), and other trace minerals (2).

The Cation Exchange Capacity (CEC) of 11 meq/100 g was determined for the raw local clay by Fernández (2012). A CEC of 19.5 meq/100 g was used for this clay, close to the reference value of 22.5 meq/100 g obtained by Baeyens and Bradbury (2004) using isotope dilution methods. Moreover, a BET surface area of 43.71 m<sup>2</sup>/g was determined for the raw clay. Assuming that most of the surface area corresponded to illite, a 77 m<sup>2</sup>/g BET area and a total site density of 2.35 meq/m<sup>2</sup> were obtained for this clay.

Batch tests were performed under different conditions by Missana et al. (2014) to obtain the individual sorption capacity of the clay by means of the partition coefficient ( $K_d$ ). The liquid phases were synthetic 0.5 NaCl solutions. Since the groundwater samples contained high concentrations of Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, which could reduce cesium sorption, the experiments were conducted with molalities up to 0.5 m K, 0.5 m NH<sub>4</sub> and 1 m Na. The raw clay and four homoionic forms were used as solid phase in order to obtain individual Cs-ion exchange capacities with competing ions.

Although  $K_d$  values increase slightly for longer contact times, most adsorption takes place during the first 2 days of contact, and the  $K_d$  values used for the geochemical model of cesium sorption were the ones obtained after 2 days. The results were interpreted according to the Bradbury and Baeyens (2000) model. The same sites were considered but the model was recalculated for high Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> concentrations. The selectivity coefficients for Cs exchange (log K) obtained with the homoionic clays can be seen in Table 1. The specific CEC for FES was determined using the inflexion point of the Na-clay sorption isotherm. The same assumption of Bradbury and Baeyens (2000) was adopted, i.e. 20% and 80% of the total CEC, for Type II and the planar sites, respectively. The model successfully predicted Cs sorption in different groundwater samples from the study site (Missana et al., 2014). For low concentrations of Cs (<1 mM), two sorption sites (FES and type II) proved to be sufficient to model all the batch experiments.

### 2.2. Column experiments

A mixture of clay and wood shavings was prepared with a weight proportion of 1:2. The wood shavings had been previously moistened to facilitate the adhesion of clay particles and to avoid segregation during mixing. In order to verify the hydraulic and geochemical performance of the filling mixture, three infiltration column tests were carried out with a Cs-137 solution. The dimensions of the column and the infiltrating flow rate were designed to obtain the variations of Cs-137 within a few weeks. They are shown in Table 2.

The hydraulic conductivity of the filling material was measured by constant head tests. Head drop between fixed points and discharge rate were measured when a steady head condition was reached. Hydraulic conductivity can thus be easily calculated by Darcy's Law. The barrier was covered with a clayish soil to prevent infiltration of surface runoff. Given the possibility that the weight of the cover could bring about compaction of the mixture and a loss of porosity and hydraulic conductivity of the filling material, the decrease in the hydraulic conductivity due to compaction was evaluated by adding several weights to the surface of the column infilling material.

In order to test the durability of the mixture and to ensure that the remains adhered to the wood shavings, suspended solids were measured at the outlet of the columns with a flow rate of about 20 m<sup>3</sup>/m<sup>2</sup>/year, which is in the high range of the flow values expected through the PRB. The outlet water was filtered with 0.45 μm filters, which were collected daily, pre-dried at 60 °C and weighed. The mass of suspended solids was calculated by measuring the weight increase in the filter.

In order to obtain the hydraulic properties of the columns, a conservative tracer test was performed in each column prior to Cs-137 injection. Thus, a pulse of 170 mL of a tritium solution was injected into each column with a constant flux (Table 2), and the activity was measured at the outlet every 2 h. The activity breakthrough curve was modeled with the code CXTFIT v.2.1 (Toride et al., 1995). The fit yields the average velocity of the tracer and the dispersion coefficient, which allow deriving the effective porosity and dispersivity of the filling material.

Following the tritium test, the Cs-137 solution was injected at the same flow rate, and samples were taken every 2 h. The activity of Cs-137 present in solution at the outlet of the columns was measured directly by means of the γ emission of the daughter Ba-137 equilibrated with a Packard Cobra II autogamma counter. Thereafter, the columns were dismantled, the solid phase divided into slices of 2–3 cm thick and weighted, and the Cs-137 activity of each slice was measured directly.

**Table 1**  
Exchange constants (log K) for Cs with respect to Na, Ca, K and NH<sub>4</sub> (Missana et al., 2014).

	Strong sites (FES)	Type II sites	Planar sites
K-X + Cs <sup>+</sup> = Cs-X + K <sup>+</sup>	4.2	2	1.2
Na-X + Cs <sup>+</sup> = Cs-X + Na <sup>+</sup>	6.9	3.1	1.8
Ca-X <sub>2</sub> + 2Cs <sup>+</sup> = 2Cs-X + Ca <sup>2+</sup>	15.3	6.7	4.7
NH <sub>4</sub> -X + Cs <sup>+</sup> = Cs-X + NH <sub>4</sub> <sup>+</sup>	4.0	1.8	1.2
Cation exchange capacity	(6 · 10 <sup>-3</sup> μeq/m <sup>2</sup> )	(0.504 μeq/m <sup>2</sup> )	(2.016 μeq/m <sup>2</sup> )

**Table 2**  
Dimensions and flow of the three infiltration column tests.

Column	C-1	C-2A	C-2B
Total mass of clay (g)	69	80	33
Column filling height (cm)	12.0	12.0	12.0
Column section (cm <sup>2</sup> )	69.4	69.4	19.6
Flow rate (cm <sup>3</sup> /h)	8.52	8.92	8.84
Equivalent Darcy flow (m <sup>3</sup> /m <sup>2</sup> /y)	10.75	11.26	39.44
Dispersivity (cm)	4.8	4.2	3.9
Porosity	0.75	0.49	0.46
Residence time (h)	73.3	45.7	12.2
Pore volume (cm <sup>3</sup> )	625	408	108
Total duration of Cs-137 injection (d)	97	140	84

### 2.3. Reactive transport modeling

Reactive transport calculations were made with the code RETRASO (Saaltink et al., 2004). The code solves simultaneously the transport equations and the chemical reactions equations. The solute transport equations express the solute mass balance per unit volume of unsaturated media. The chemical equations solve the aqueous speciation and the mass transfer of each component between the aqueous phase and the exchange complex. The coupled differential equations describing the balance of mass of the components in 1D problem can be written as:

$$\theta \frac{\partial C_j}{\partial t} = -q \frac{\partial C_j}{\partial z} + D \frac{\partial^2 C_j}{\partial z^2} + R_j \quad (1)$$

where  $\theta$  is the porosity,  $C_j$  is the total dissolved concentration of the  $j^{\text{th}}$  component,  $z$  is the distance along the column edge,  $t$  is the time,  $q$  is the darcy velocity,  $D$  is the dispersion coefficient and  $R_j$  is the mass of the  $j^{\text{th}}$  component supplied or removed to/from the solution by the exchange reactions. The dispersion-diffusion coefficient  $D$ , is defined according to Bear (1979) as:

$$D = \frac{\alpha q}{\theta} + D_e \quad (2)$$

where  $\alpha$  refers to the hydraulic dispersivity along the column axes, and  $D_e$  is the effective diffusion coefficient, which has been neglected for the flow values used in the column experiments.

Aqueous speciation has been solved assuming instantaneous equilibrium among all aqueous species. Then, the Mass-Action Law relates aqueous species among them and allows to select a set of aqueous primary species (one for each component), and express the rest of aqueous species as a function of these primary species.

Cation exchange reactions have been formulated according to the Gaines–Thomas convention:

$$\frac{1}{z_i} I^{z_i} + \frac{1}{z_j} (X_{z_j} - J) = \frac{1}{z_i} (X_{z_i} - I) + \frac{1}{z_j} J^{z_j} \quad (3)$$

where  $z$  is the electric charge of the cation, and  $(X-I)$  and  $(X-J)$  denote the exchangeable site occupied by the I and J ions, respectively. Chemical equilibrium between the aqueous and exchangeable species has been assumed, and a Mass Action Law formulated:

$$K_{I/J} = \frac{a_j^{\frac{1}{z_j}} a_{X-1}^{\frac{1}{z_i}}}{a_i^{\frac{1}{z_i}} a_{X-J}^{\frac{1}{z_j}}} \quad (4)$$

where  $a_i$  is the activity of the  $i$ -aqueous species calculated according the extended Debye–Huckel expression, and  $a_{X-1}$  is the activity of the exchangeable species equated to the equivalent fraction.

To solve the three column cases, a 1D numerical grid of 24 equidimensional elements was defined. At the inflow boundary, a flow (Table 2) and concentration was imposed (Table 3). Transport parameters ( $\theta$  and  $\alpha$ ) were those obtained from the tracer tests as described below.

To solve the geochemical problem, a set of 11 primary aqueous species (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cs<sup>+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>), 15 secondary aqueous species (OH<sup>-</sup>, CaCl<sup>+</sup>, CaCl<sub>2</sub>, CaOH<sup>+</sup>, CaSO<sub>4</sub>, MgCl<sub>2</sub>, Mg<sub>4</sub>OH<sup>4+</sup>, MgSO<sub>4</sub>, NaCl, NaOH, NaSO<sub>4</sub><sup>-</sup>, KCl, KSO<sub>4</sub><sup>-</sup>, HCl, CsCl) and 5 exchanged species (X–Na, X–K, X–Cs, X–NH<sub>4</sub>, Ca–X<sub>2</sub>) were considered. The equilibrium constants for the aqueous speciation reactions were those recorded in the WATEQ database (Ball and Nordstrom, 1991). The equilibrium constant exchange reactions were obtained from batch experiments and are plotted in Table 1.

The value of the exchange capacity of the mixture was the objective to calibrate. Owing to the low Cs-137 activity of the inflow solutions, only two sorption sites (FES and type II) were considered. The initial guessed value for each of these two site types (CEC in μeq/L) was calculated according to:

$$CEC = \frac{M \cdot w \cdot S \cdot c}{V_p} \quad (5)$$

where  $M$  is the mass of clay in the column (Table 2),  $w$  is the weight fraction of illite in the clay (0.57),  $S$  is the illite specific surface (77 m<sup>2</sup>/g),  $V_p$  is the pore volume of the column (Table 2), and  $c$  is the CEC of each sorption site of illite (μeq/m<sup>2</sup>) (Table 1).

**Table 3**  
Mean concentrations of inflow solutions for the three columns (mg/L).

Column	C-1	C-2A	C-2B
Br <sup>-</sup>	19	–	–
Cl <sup>-</sup>	4534	17,750	17,750
SO <sub>4</sub> <sup>2-</sup>	1878	–	–
NO <sub>3</sub> <sup>-</sup>	6.6	–	–
HCO <sub>3</sub> <sup>-</sup>	134	–	–
NH <sub>4</sub> <sup>+</sup>	209	–	–
Ca <sup>2+</sup>	590	–	–
Mg <sup>2+</sup>	98	–	–
Na <sup>+</sup>	2657	11,500	11,500
K <sup>+</sup>	549	–	–
pH	7.2	6.7	6.7
Cond (mS/cm)	14.3	48.1	48.1
Cs-137 (Bq/m <sup>3</sup> )	7.15 · 10 <sup>4</sup>	7.15 · 10 <sup>4</sup>	7.15 · 10 <sup>4</sup>

### 3. Results and discussion

#### 3.1. Hydraulic properties

The results of the constant head tests are shown in Fig. 1. The original mixture shows a high hydraulic conductivity that drops slightly when increasing confining pressure (from  $4 \times 10^{-4}$  to  $1 \times 10^{-4}$  m/s). These values are higher than those of most aquifers (Domenico and Schwarz, 1998). In particular, the measured hydraulic conductivity is always higher than those values measured for the different layers of wastes measured at the field site in SW Spain (Carretero and Suso, 2009). Therefore, the barrier would meet the requirement of being more permeable than the surrounding rocks, i.e. flux through the barrier would be facilitated.

One may think that the higher the clay: wood shavings, the higher Cs retention of the barrier. However, there is a limitation for the mass of clay particles stuck onto the wood shavings. Then, the suspended solids in the outflow of the columns were measured for 30 days, averaging  $0.5 \pm 0.2$  mg/day. This is equivalent to a loss of less than 0.3% of the original clay mass per year. Therefore, the mixture was considered sufficiently stable for more than two years. Preliminary tests with higher proportions of clay with respect to wood shavings were also performed, and these experiments led to much higher clay detachment and suspended matter. Therefore, the optimum weight proportion of clay:wood shavings 1:2 was finally established.

A tritium tracer test was performed in each column. For the sake of simplicity, only the results of test performed in column 2A are plotted in Fig. 2. Also the best fit obtained with the code CXTFIT v.2.1 is also plotted. The peak of the tritium elution curve appears after 45.8 h. Taking into account an injection flow rate of  $8.92 \text{ cm}^3/\text{h}$ , the total volume eluted is  $409 \text{ cm}^3$ , which represents a fraction of 0.49 of the total volume of the column (Table 2). The best fit for an average Darcian flow velocity of  $0.128 \text{ cm}^3/\text{cm}^2/\text{h}$  was obtained for a dispersion coefficient of  $0.5 \text{ cm}^2/\text{h}$ . According to equation (2), this yields a dispersivity value of 1.9 cm. Column 1 contained a filling that was less compacted than those of 2A and 2B and a distinctly higher porosity of 0.75 was obtained. Tracer test data for the two other columns (not shown) are treated similarly. The hydraulic parameters of the three columns are listed in Table 2.

#### 3.2. Reactivity: Cs sorption properties

The reactivity of the clay to retain Cs was tested through previous batch experiments (Missana et al., 2014). The aim of the column experiments was to test the Cs sorption efficiency in a flow

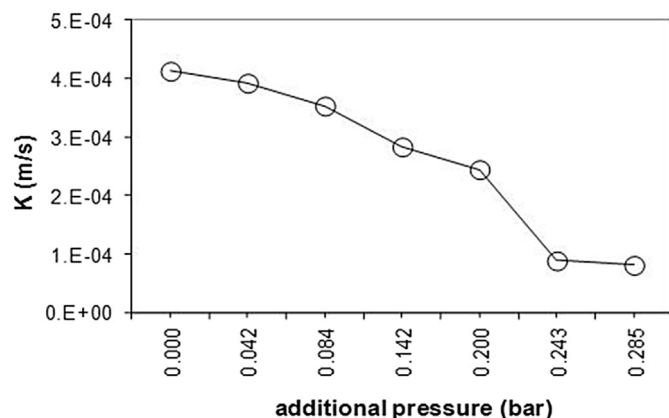


Fig. 1. Hydraulic conductivity variation with confining pressure for clay: wood shavings mixture.

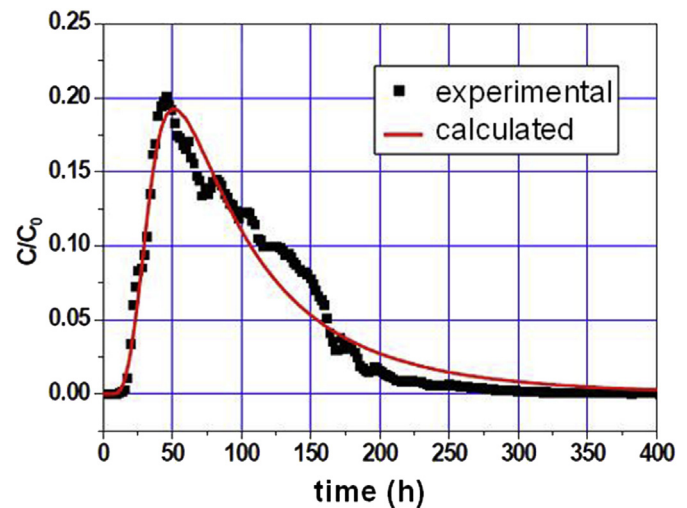


Fig. 2. Breakthrough curve of tritium at the outlet of column 2A. The fitting curve was calculated with the code CXTFIT.

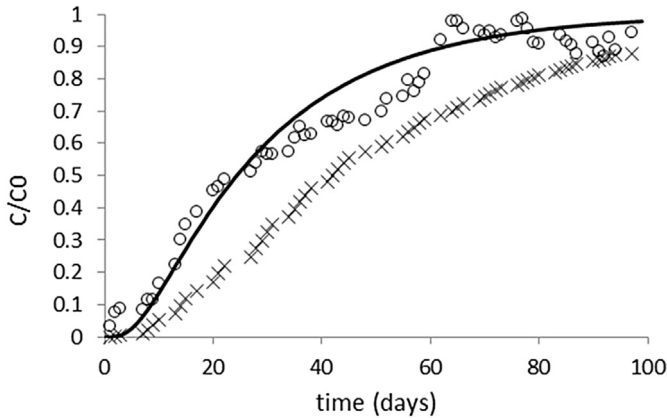
through setting, and to supply quantitative data to calibrate a reactive transport model. Essentially, the parameter to fit is the effective CEC value of the column infilling material. As described above, the initial guess of the CEC was calculated following equation (5). Then, the CEC value was slightly modified when modeling in order to obtain the best fit between the calculated and the experimental values. The final CEC values compared with those expected from equation (5) are listed in Table 4.

Groundwater samples from the site contain high concentrations of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ . These cations compete for the same sorption sites and could reduce cesium sorption. Therefore, column 1 was used with real groundwater (Table 3) to test these competing effects. Fig. 3 shows the evolution of relative activity ( $C/C_0$ ) of Cs-137 in the outflow of column 1, together with the predicted breakthrough curves. The blind prediction (using CEC value from equation (1)) for column 1 slightly under-predicts the Cs retention in the column. However, in spite of the complex water used, the blind prediction describes the trend of the breakthrough curve, and the difference between the calculated and fitted CEC values is only 6% (Table 4).

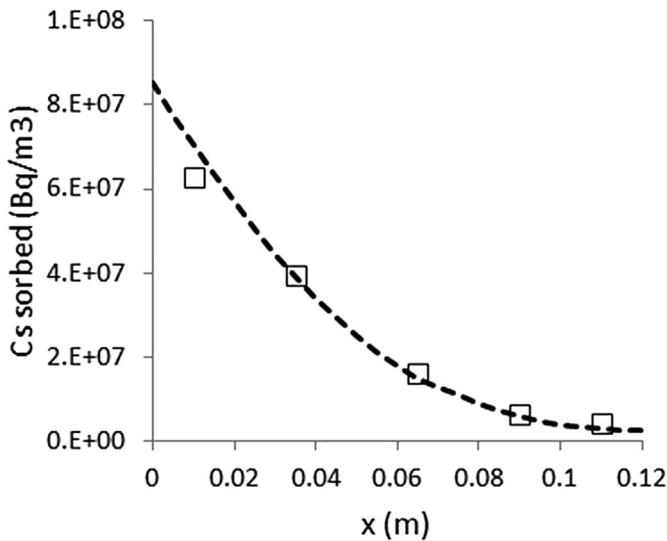
The objective of columns 2A and 2B was to study the effect of different residence times and packing of the reactive material (Table 2). Synthetic Cs-137-containing NaCl solutions were used (Table 3). No Cs-137 activity was detected at the outlet during the tests in Columns 2A and 2B. Because of the lack of strongly competing ions Cs-137 was very efficiently sorbed to the reactive filling, and no Cs-137 was detected in the outflow solution in reasonable experimental times. In order to obtain experimental retention data, the infilling material was cut into slices and the activity of the Cs-137 adsorbed during the test was measured in the solid phase. The experimental results, together with the predicted values are shown in Figs. 4 and 5. Column 2A was satisfactorily modeled with the CEC values calculated from equation (5), and the trend predicted with CEC values from equation (5) perfectly matches the experimental Cs-137 activities measured in the solid phase (Fig. 4). However, the blind prediction over-predicts the experimental values for column 2B, especially at the inlet of the column. The differences between the blind and calibrated predictions is +13%. The accuracy of the prediction is poorer than in column 1 and 2A. This could be due to a less accurate estimation of porosity and/or to the difficulty of cutting slices with equal clay: wood shavings proportion for the smallest column.

**Table 4**  
Total CEC of FES and Type II sites (eq/L) predicted from the mass of clay and the sorption model compared with the values used to fit the experimental values from the three columns.

	Theoretical		Experimental		Difference %
	FES	type II	FES	type II	
Column 1	3.61E-05	3.04E-03	3.40E-05	2.86E-03	-6.0
Column 2A	8.65E-05	7.26E-03	8.65E-05	7.26E-03	0.0
Column 2B	1.32E-04	1.11E-02	1.60E-04	1.26E-02	13.6



**Fig. 3.** Comparison between measured (points) and predicted (continuous line) C/Co of Cs-137 activity at the outlet of column 1, which contained high concentrations of Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> (Table 3), which compete for sorption sites.

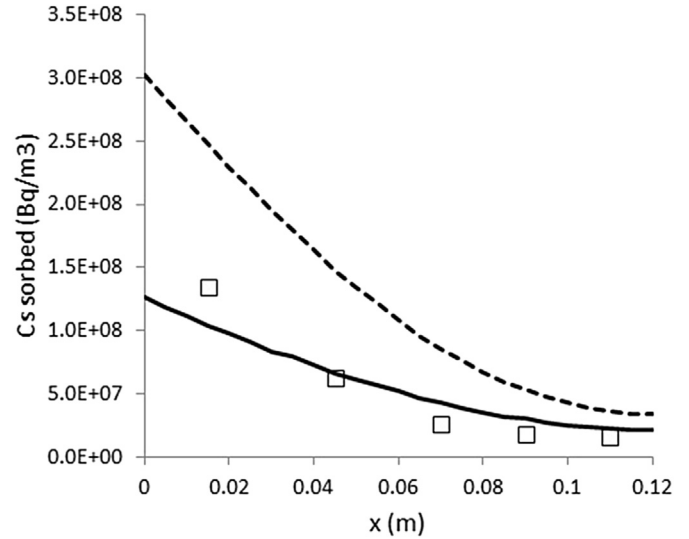


**Fig. 4.** Comparison between measured (points) and predicted (continuous line) activity of Cs-137 remaining in the solid phase of column 2A after 140 days of experiment.

The performance of the final barrier will be measured from the Cs-137 activity in the outflowing water, rather than from the Cs-137 distribution inside the infilling material. Therefore, the accuracy expected for the blind prediction of the performance of a reactive barrier can be assumed closer or lower than 10%.

**4. Design of a permeable reactive barrier**

Once validated with the column experiments, the reactive transport model was used to predict the evolution of <sup>137</sup>Cs



**Fig. 5.** Comparison between measured (points) and predicted (continuous line) activity of Cs-137 remaining in the solid phase of column 2B after 84 days of experiment.

concentration downstream from a hypothetical barrier. The main parameters for this basic simulation are shown in Table 5. The first conceptual model considered a barrier 2 m thick and a filling material with a weight proportion of clay:wood shavings of 1:2. Since the pressure of the overlying soil will probably compact the filling material, a porosity of 0.5 close to that of columns C2A and C2B was assumed instead of 0.7 of column C1. The concentration to be treated in groundwater was defined as 10<sup>5</sup> Bq/m<sup>3</sup> of <sup>137</sup>Cs, which was the highest value found in the study area. A flux of 10 m<sup>3</sup>/m<sup>2</sup>/yr was assumed for the different scenarios, which is in the order of magnitude of the expected flow at the site. The water of column experiment C1 was assumed as inflow water for the calculations because it corresponded to an actual sample from a borehole upstream of the projected barrier location.

The results of the calculations under the base case parameters are plotted in Fig. 6 (thick line). The upper limit of Cs-137 concentration in drinking water is 10<sup>4</sup> Bq/m<sup>3</sup>. Although this concentration is not the aim of this study, it will be used to describe the performance of the barrier. Thus, as shown in Fig. 6, the effluent

**Table 5**  
Parameters for the base simulation case of a permeable reactive barrier.

Barrier width (m)	2.0
Estimated porosity	0.5
Exchange capacity: FES (eq/L)	8.65E-05
Exchange capacity: type II sites (eq/L)	7.26E-03
Darcy equivalent flow (m <sup>3</sup> /m <sup>2</sup> /y)	10.0
Residence time (days)	36.5
Inflow solution:	C-1 (Table 2)
K (mg/L)	740
NH <sub>4</sub> (mg/L)	337
Cs-137 activity (Bq/m <sup>3</sup> ) in inflow solution	10 <sup>5</sup>

concentration will exceed  $10^4$  Bq/m<sup>3</sup> of Cs-137 after 23 months in operation under the conditions of the base case. A longer duration can be achieved with a thicker barrier. The proportion is linear, i.e. a 2 m barrier will last 46 months before the reference limit is exceeded.

As some groundwater parameters in the study area are uncertain or variable, additional calculations were performed to study the effect of this uncertainty on Cs-137 concentrations downstream of the barrier. The sensitivity of the model was studied with respect to the clay: wood shavings proportion, barrier width, and Cs-137, K and NH<sub>4</sub> concentrations in the inflow. The results of the sensitivity calculations are also plotted in Fig. 6.

As expected, arrival time scales linearly with the inverse of Darcy's flux (Litchner, 1993). Thus, when using flow rates of 20 and 5 m<sup>3</sup>/m<sup>2</sup>/yr, twice and half the base case, the reference limit of  $10^4$  Bq/m<sup>3</sup> is exceeded in 11.5 and 46 months, respectively. The same linear behavior can be observed when doubling or halving the CEC of the filling material (Fig. 6A). An improvement in the sorption capacity can be achieved by increasing the clay: wood shavings proportion of the mixture, although that of 1:2 used in the calculations is close to the optimum to prevent clay detachment and suspended matter.

Variation in the concentration of <sup>137</sup>Cs in the inflow water does not have a linear behavior. With values of  $10^6$  Bq/m<sup>3</sup> (ten times higher than those of the base case), the time elapsed with outflow concentrations lower than the reference limit ( $10^4$  Bq/m<sup>3</sup>) decreases to 16 months. This is some two thirds of the time elapsed in the base case (Fig. 6D). Likewise, for  $10^7$  Bq/m<sup>3</sup> concentrations (one hundred times higher than the initial case) the elapsed time with outflow concentrations lower than the reference concentration ( $10^4$  Bq/m<sup>3</sup>) is reduced to 13 months, slightly more than half the base case time. This shows a higher efficiency of the barrier for high concentrations of <sup>137</sup>Cs, which is consistent with a higher sorption of <sup>137</sup>Cs versus other cations competing for the exchange positions.

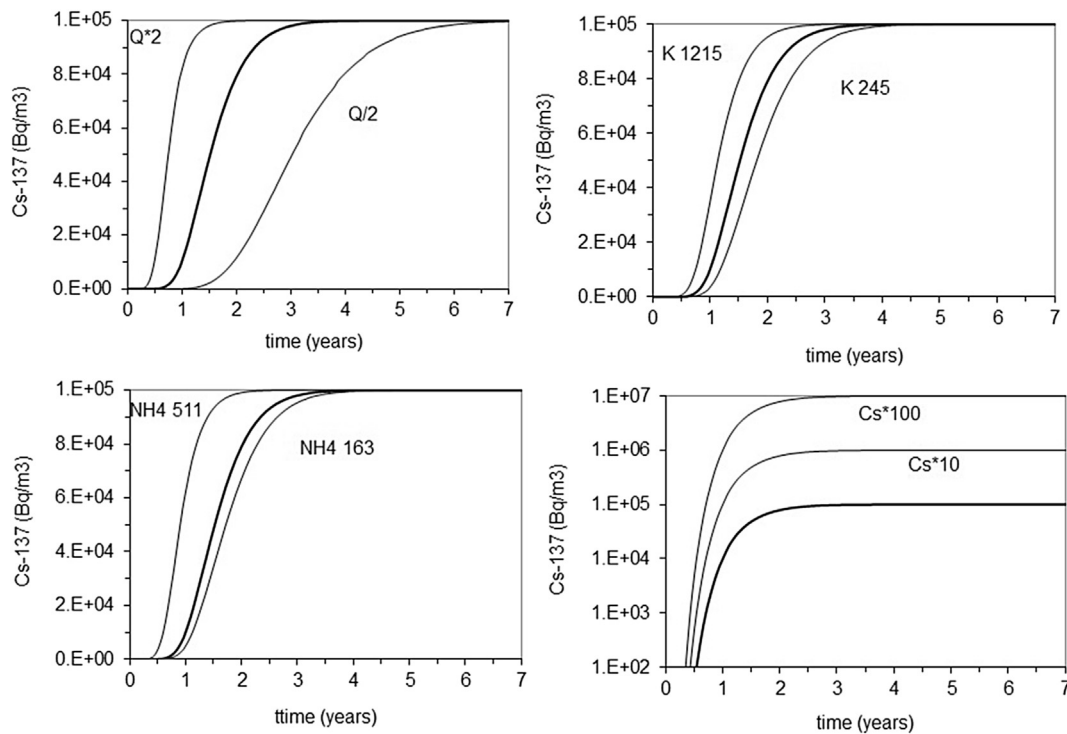
The concentrations of K<sup>+</sup> in the samples from the study area range from 245 to 1215 mg/L with an average of 740 mg/L. Those of NH<sub>4</sub> range between 163 and 511, with an average of 337 mg/L (over 398 analyses). Both K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> show no correlation in the study area. The range of variation of K and NH<sub>4</sub> concentrations in the inflow induces uncertainty ranges in the time elapsed with concentrations lower than the reference limit from 19 to 29 months for K<sup>+</sup>, and from 18.5 to 31 months for NH<sub>4</sub><sup>+</sup> (Fig. 6C). Given the lower affinity for the sorption sites of illite (log K in Table 1), variations in the concentration of Ca and Na in the inflow water have little effect on the retention of <sup>137</sup>Cs.

## 5. Conclusions

The mixture of wood shavings and clay (from 2:1 to 1:1 by weight) is a material that has a sufficiently high hydraulic conductivity to ensure a satisfactory hydraulic performance for an eventual permeable barrier excavated in most aquifer materials. The large proportion of clay ensures a high retention capacity for Cs. The clay must be completely dried, ground and sieved before mixing with the shavings. The shavings must be moistened previously with water to ensure the adherence of clay to their surface.

This concept is going to be tested at a real case of <sup>137</sup>Cs pollution in a building and industrial waste repository in SW Spain. The clay 'Rojo Carboneros', used in brick factories, with 57 wt% illite was studied through column experiments. The Cs-137 activity at the outlet and inside the columns filled with the reactive material was systematically analyzed. A reactive transport model using the cation exchange model of Bradbury and Baeyens (2000), extended to high K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> concentrations, predicted the experimental results satisfactorily.

The model was used to predict the performance of a hypothetical 2 m thick barrier with versus a real solution containing  $10^5$  Bq/m<sup>3</sup> Cs-137 and K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> concentrations as high as 740 and



**Fig. 6.** Breakthrough curves of Cs-137 activity computed at the outlet of a 2 m thick barrier. The thicker curve corresponds to the base case using the parameters listed in Table 5, and the thinner curves represent modifications of the base case: A) Cation Exchange Capacity (CEC) and Darcy flux ( $q$ ) half and twice the base ones; B) Lower and upper values of K concentration (mg/L) recorded in the study area; C) Idem NH<sub>4</sub>; D) Hypothetical higher Cs-137 concentrations in the inflow solution.

337 mg/L, respectively. The calculations predict  $^{137}\text{Cs}$  activities lower than the drinking water limit ( $10^4 \text{ Bq/m}^3$ ) in the outflow water for 23 months. This time span can be increased linearly with a thicker barrier, a higher clay: wood shavings proportion or a lower Darcian flow. The barrier treats high concentrations of Cs-137 more efficiently since its operation time decreases linearly with the logarithm of the inflow Cs-137 concentrations. This means that when increasing Cs-137 concentrations by one order of magnitude, the operation time of the barrier decreases by less than one third. Finally, the performance of the barrier is very sensitive to the concentration of competing cations K and  $\text{NH}_4$ . The barrier will probably last longer in most hydrochemical environments given that the concentrations used in the experiments and calculations are very high.

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