

Design of a Permeable Reactive Barrier to Retain Cs-137: Laboratory Experiments

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INTRODUCTION

Cs-137 is one of the main products of the nuclear fission of Uranium-235 or Plutonium-239. It is usually disposed in High Level Radioactive Waste (HLRW) repositories which have to prove to provide permanent isolation. However, sometimes radionuclides can be released to the environment by leakage of nuclear installations such as Hanford Site (Smoot. et al, 2011) or accidents like Chernobyl (The Chernobyl forum, 2005).

The retention of cesium has been studied on different minerals to evaluate them as possible materials for reactive barriers (Krumhansl et al, 2001). Sorption of Cs-137 by different clay rocks has been studied in depth by Bradbury and Baeyens (2000), Zachara et al. (2002) and Liu et al (2003). All these authors conclude that illite is the main responsible for cesium sorption. Among the cations present in water only K, NH₄ and compete efficiently with Cs-137 for the same sorption sites.

Up to now, clay to control Cs-137 contamination has been designed as low-permeability barriers to prevent groundwater flow and seal the polluted area. In certain cases, however, the isolation is difficult and it could be necessary to treat the groundwater flow.

Permeable Reactive Barriers (PRB) is an in situ remediation method for groundwater that make possible to avoid its migration to surface waters or aquifers. Its design is based on digging a trench and filling it up with adequate material. treatment PRB requires filling materials to be:

- 1) reactive, able to form an insoluble solid phase with the species of

interest solved in water;

- 2) permeable, so they allow water flux through it, acting as a filter;
- 3) passive, so they work with natural energy (gravity), without need of continuum supervision;
- 4) inexpensive and accessible, as huge filling material volumes are involved.

In the present work, we propose a PRB based on the adsorption of Cs-137 on illite-rich clays to treat a case of polluted groundwater from an industrial repository. Usually, a fine grain size, such as that of clays, is associated with very low permeability. However, we propose as a filling material a powdered clay rock from the surrounding area dispersed on the surface of wood flakes. In the present work we test the permeability and reactivity of this new filling material by means of laboratory batch and column tests combined with reactive transport modeling.

HYDRAULIC PERMEABILITY

As a first design approximation for the reactive barrier, a mixture of wooden shavings, as porous matrix, and clay as reactive material has been proposed. Wooden shavings have been moistened previously to facilitate the physical adhesion of the clay particles on them and to avoid the segregation of both materials during the mixture. Tests have been performed with a weight proportion of clay:shavings:water 1:2:3. Volumetrically, 100 g of clay have been distributed on a total mixture volume of 850 mL. To measure hydraulic conductivity, constant head tests have been used. The measurement is based on Darcy's Law:

$$Q = A K d h \quad (1)$$

where Q is the infiltration flow, A the column section where flux flows through, K hydraulic conductivity and dh the piezometric height gradient.

It is foreseeable that the barrier might be covered with clay or clayish soil to isolate it and avoid infiltration of surface runoff. Therefore, the effect of different confining pressures equivalent to up to 1m of soil with a 30% of porosity have been tested (Fig. 1).

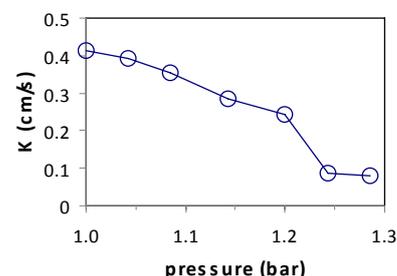


fig. 1 Hydraulic conductivity variation with confining pressure.

SORPTION PROPERTIES

As the aim of the filling material is to be economic and easy to obtain, a local sediment containing illite (40%) has been tested in order to obtain its specific cesium partition coefficient (K_d). K_d values has been obtained putting in touch a weighed amount of solid material with a volume of 6 local waters variable K concentrations. Cs-137 was added, and the K_d values (mL/g) were obtained as:

$$K_d = \frac{C_0 - C_f}{C_f} \cdot \frac{V}{M} \quad (2)$$

where C₀ is the initial radionuclide concentration spiked (Bq/mL), C_f radionuclide final concentration in

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solution (Bq/mL), V liquid volume (mL) and M solid mass (g). Solid-water contact time was 1day, the shortest estimated residence time of water in the barrier (worst case scenario). Kd values increase slowly for longer times.

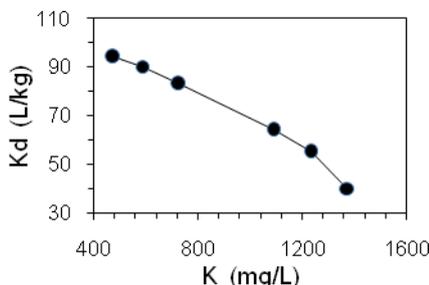


fig. 2. Variation of specific sorption of clay potassium concentration.

The sorption model used for the geochemical modeling has been the one proposed by Bradbury and Baeyens (2000), considering three sorption sites with different affinities for cesium. This model also considers the competition of K, Na, Ca and NH4 for the same sorption sites as cesium. These authors also established a Cation Exchange Capacity (CEC) of 0.2 eq./kg for illite, which is distributed in 0.25% for high affinity sites, 20% for type II sites and the rest for planar sites.

Reactions	High Aff.	Med. Aff.
$K-X + Cs^+ = Cs-X + K^+$	4.0#	1.5
$Na-X + Cs^+ = Cs-X + Na^+$	7.0	3.6
$Ca-X_2 + 2Cs^+ = 2Cs-X + Ca^{2+}$	2.4	2.1
$NH_4-X + Cs^+ = Cs-X + NH_4^+$	4.1*	1.1*
Exch. capacity (eq./kg)	$5e^{-2}$	$4e^{-4}$

Table 1: Parameters of sorption modeling from Bradbury and Baeyens (2000); (*) Zachara et al. (2002); (#)Recalibrated, present work.

Owing to the exchange coefficients of the model were obtained from experiments with K concentrations lower than 200 mg/L, the value of the Cs-K exchange coefficient was recalibrated with the measured Kd values. The Kd values predicted by the model compare reasonably well with the experimental values (Fig. 3).

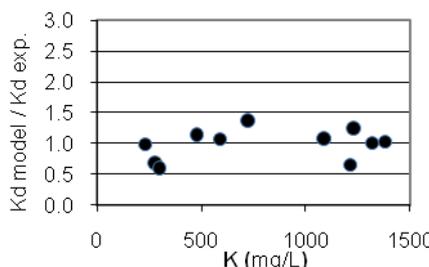


fig. 3. Comparison between experimental and calculated sorption values.

COLUMN EXPERIMENTS

In order to verify the hydraulic and geochemical performance of the filling mixture, two infiltration column tests have been performed done with a solution with spiked with Cs-137 Table 2).

	C 1	C 2
Estimated porosity	0.5	0.5
Column height (cm)	16.0	16.0
Column section (cm ²)	69.4	19.6
Flow rate (cm ³ /h)	8.6	8.6
Equivalent Darcy flow (m ³ /m ² /y)	10.9	38.4
Residence time (h)	1.1	0.3
K in the Inflow solution (mg/L)	727	1091
Cs-137 activity in Inflow solution (Bq/m ³)	10 ⁷	10 ⁷

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

The Cs-137 activity of the outflow has been measured directly by means of the γ emission autogamma counter. With the aim of validating the geochemical Cs sorption model in a flow context, a reactive transport model has been used to simulate the infiltration column.

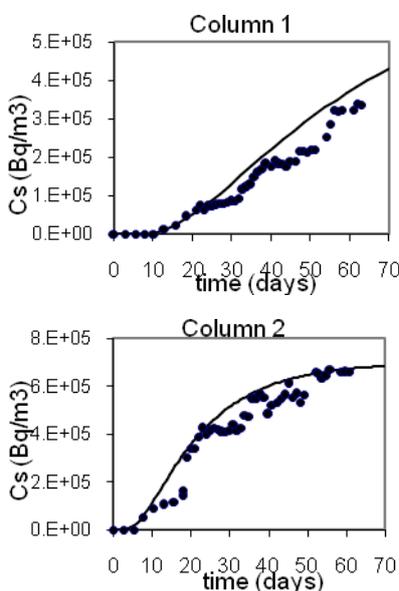


fig. 4. Comparison between measured (points) and predicted (continuous line) ¹³⁷Cs activity at the outlet of the columns.

Reactive transport calculations have been done with RETRASO (Saaltink et al., 2004). Fig. 4 compares satisfactorily the results of the geochemical model with the experimental values obtained with the two infiltration tests.

CONCLUSIONS

The mixture of wooden shavings and clay (2:1 by weight) is a material that has a high enough hydraulic conductivity (10⁻⁴ m/s) to ensure an adequate hydraulic performance for an eventual permeable barrier excavated in the study area.

This clay has approximately 40% of illite, a mineral whose affinity to retain Cs-137 is high and has been studied experimentally. A residence time of 1 h of water in the barrier is enough to reach a retention rate close to the maximum (equilibria). The sorption model proposed by Bradbury and Baeyens (2000), calibrated for lower potassium concentrations than in our study area, predicts an excess of Cs-137 sorption with respect to the values observed in batch experiments. The model recalibrated with these batch experiments allowed to predict very satisfactorily the activity of Cs-137 at the outlet of two infiltration columns. This permits to predict the behavior of a hypothetical barrier filled with these clay-shavings mixture by means of a reactive transport model.

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