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Journal of Contaminant Hydrology 47 (2001) 127–137

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JOURNAL OF
**Contaminant
Hydrology**

Solute transport properties of compacted Ca-bentonite used in FEBEX project

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Received 18 August 1999; received in revised form 25 February 2000; accepted 31 March 2000

Abstract

The present Spanish concept of a deep geological high level waste repository includes an engineered clay barrier around the canister. The clay presents a very high sorption capability for radionuclides and a very small hydraulic conductivity, so that the migration process of solutes is limited by sorption and diffusion processes. Therefore, diffusion and distribution coefficients in compacted bentonite (i.e. in “realistic” liquid to solid ratio conditions) are the main parameters that have to be obtained in order to characterise solute transport that could be produced after the canister breakdown.

Through-Diffusion (TD) and In-Diffusion (ID) experiments with HTO, Sr, Cs and Se were carried out using compacted FEBEX bentonite, which is the reference material for the Spanish concept of radioactive waste disposal. Experiments were interpreted by means of available analytical solutions that allow the estimation of diffusion coefficients and, in some cases, distribution coefficients. Analytical solutions are simple to use, but rely on hypotheses that do not hold in all the experiments. These experiments were interpreted also using an automatic parameter estimation code that overcomes the limitations of analytical solutions. Numerical interpretation allows the simultaneous estimation of porosity, diffusion and distribution coefficients, accounts for the role of porous sinters and time-varying boundary concentrations, and can use different types of raw concentration data. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diffusion; Sorption; Bentonite; Radionuclides

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1. Introduction

Bentonite is a swelling clay due to its content of the smectite clay mineral montmorillonite, and it is considered as a potential back-fill material in high level nuclear waste repositories because of its very high sorption capability and an extremely low permeability. Since at the repository conditions the hydraulic gradient will be low, the migration of contaminants in compacted bentonite is expected to be a diffusion-controlled process, generally retarded by sorption. Diffusive transport of radionuclides in clay porewater depends on the charge, ionic size, dipolar momentum and polarizability of the diffusing species. The determination and the understanding of both diffusion and sorption properties of this clay is a very important issue for the analysis and consideration of many processes that may affect safety of an underground disposal of nuclear waste.

The sorption capability is usually described by the K_d concept. K_d s represent a mixture of processes whose averaged contribution gives a ratio between the concentration of a substance in the solid and aqueous phases. There are many processes embedded within the K_d value such as ion exchange, surface complexation and redox reactions. Therefore, the K_d concept is a poor representation of the chemical interactions between bentonite and water if the experimental conditions do not approach the real ones as, for example, in batch experiments.

One of the main goals of the present work deals with the determination of K_d values under realistic solid/liquid ratios for some of the most relevant radionuclides. Several diffusion experiments have been carried out using Through-Diffusion (TD) and In-Diffusion (ID) tests that have been interpreted using the analytical solutions proposed by Wolfrum et al. (1988) and Put and Henrion (1992), as well as numerical tools such as CORE-LE (Samper et al., 1998) and INVERSE-CORE-LE (Dai and Samper, 1999).

Interpretation by means of available analytical solutions allows the estimation of diffusion coefficients. K_d s can be estimated only in special cases, mainly due to uncertainties on the diffusion-accessible porosity, which is different for each species (Carrera et al., 1991). Analytical solutions are simple to use, but rely on simplifying hypotheses such as infinite length of columns and constant boundary concentrations, which do not hold in all the experiments. Limitations of the analytical methods are overcome by resorting to numerical methods. Diffusion experiments were interpreted using an automatic parameter estimation code, INVERSE-CORE-LE, a code which incorporates the solution of the inverse problem into a previous water flow and reactive transport code CORE-LE which has been also applied to hydrochemical reactive transport through aquitards (Xu et al., 1999). The solution of the inverse solute transport problem in INVERSE-CORE is based on minimizing a calibration criterion that measures the weighted difference between computed and measured concentrations. Early versions of the code used a Golden Section search method, which is not efficient for complex problems involving many parameters. The latest version of the code uses a Gauss–Newton–Levenberg–Marquardt algorithm that shows a fastest convergence. For the interpretation of these experiments, the Golden Section method was used during preliminary runs while the Gauss–Newton–Levenberg–Marquardt algorithm was used to produce the final results.

Numerical methods account easily for the role of porous sinters and time-varying boundary concentrations and allow the simultaneous estimation of porosity, diffusion and distribution coefficients in an efficient and objective manner by using different types of data such as concentrations in upstream and downstream reservoirs, dissolved and total tracer concentrations. Here, both analytical and numerical interpretation methods were used to interpret diffusion experiments. This enabled us to: (1) test the estimation capabilities of numerical methods, and (2) to identify the main limitations of analytical methods. For instance, failing to account for the role of sinters may lead to erroneous effective diffusion coefficients which may overestimate true values by a factor of 2.

2. Materials and methods

2.1. Materials

The clay used in all the experiments is FEBEX bentonite, which comes from the Cortijo de Archidona (Almería, Spain) deposit. FEBEX bentonite has a smectite content greater than 90% ($93 \pm 2\%$), with quartz ($2 \pm 1\%$), plagioclase ($3 \pm 1\%$), cristobalite ($2 \pm 1\%$), potassic feldspar, calcite and trydimite as accessory minerals. An exhaustive description of this clay can be found elsewhere (ENRESA, 1998). The water used in all experiments was a synthetic groundwater in equilibrium with the clay. The composition of the synthetic water is shown in Table 1.

The tracers used were HTO (tritiated water), selenium(IV), strontium and cesium. HTO was used as a conservative tracer because it is expected to behave similarly to all those elements that do not show retention or interactions with the solid phase. The ^{79}Se isotope (half-life 6.5×10^4 years) has been identified as one of the key nuclides contributing to the long-term risk of geological disposal. ^{90}Sr is potentially one of the most hazardous fission products from the spent uranium fuel during the first 200–300 years after discharge. ^{137}Cs is a fission product typically present in nuclear wastes.

TD experiments were carried out using HTO and strontium and ID experiments with cesium and selenium. All the experiments were performed under oxic conditions.

Table 1
Chemical composition of the synthetic water

Element	(mg/l)
SO_4^-	14
F^-	0.18
Cl^-	12
NO_3^-	3.5
HCO_3^-	148
Ca^{2+}	47
Mg^{2+}	10
Na^+	15
K^+	1.1
SiO_2	20
pH	8.3
Cond. ($\mu\text{S}/\text{cm}$)	282

2.2. Methods

2.2.1. TD experiments

Bentonite cylindrical plugs of different dry densities, 5.3 or 8.3 mm thick and with a diameter of 5 cm, located in a stainless steel high pressure cell and sandwiched by sintered stainless steel filters, were saturated during 4 weeks prior to the experiment. The water content in bentonite indicates if the plug is saturated (47.7, 36.5 and 24.6 wt.% for the density of 1.18, 1.36, 1.62 g/cm³, respectively), and the minimum time needed for saturation has been determined by previous experiments.

The cells separated two deposits of synthetic groundwater: the Inlet (IN) deposit, where the tracer was added, and the Outlet (OUT) deposit. The solutions were maintained at constant stirring until the end of the experiment and the tracer concentration in solution was measured in both deposits at regular intervals. TD experiments with HTO were performed with clay plugs at different dry densities in order to study the effects of the compaction degree on the diffusion processes.

Generally, in the experimental set up of TD tests, the concentration of tracer in the IN reservoir is maintained constant during the experiments. In fact, with this boundary condition, an analytical solution for the Fick's first law can be used to obtain diffusion coefficients when the steady-state is reached (Crank, 1975). Anyway, one of the main difficulties of this kind of experiments is to keep the IN concentration constant for the long periods of time needed to complete the experiment.

An alternative method for the determination of diffusion coefficients from TD experiments is based on Fick's second law and was proposed by Wolfrum et al. (1988). With this method, temporal concentration variations in both reservoirs are allowed and the apparent diffusion coefficient, D , can be estimated from the following formula:

$$D = \frac{\ln[\Delta C_0/\Delta C]}{\beta t} \quad (1)$$

where ΔC is the concentration difference between the two reservoirs at time t . ΔC_0 is the initial concentration difference between the two reservoirs. β is $A/d(1/V_a + 1/V_i)$, where V_a , V_i are the volumes of the reservoirs, A is cross-sectional area of the clay plug, and d is the thickness of the clay plug.

Eq. (1) evaluates apparent diffusion coefficients by using the concentration differences between the reservoirs and therefore includes observations of both sides of the clay plug. Therefore, this method enables to distinguish the processes due to the initial sorption (loading) and subsequent diffusive phases. Diffusion coefficients can be obtained by a linear regression of the experimental data representing $\ln[\Delta C_0/\Delta C]$ vs. βt . In this representation, the apparent diffusion coefficient is the slope of the straight line obtained.

TD experiments were simulated with the numerical approximation, considering five different regions: the IN reservoir, the first sinter, the clay plug, the second sinter and finally the OUT reservoir. The diffusion coefficient in the reservoirs is assumed to be high enough to have all the nodes in the reservoirs with the same concentration. The initial concentration in the IN reservoir is equal to the initial tracer concentration. In the sinters, the clay and the OUT reservoir, the initial concentration is equal to zero.

2.2.2. ID experiments

Clay plugs of a dry density of 1.65 g/cm^3 with 38 mm of diameter and either 25 or 50 mm of length were compacted in a stainless steel ring prior to be located into stainless steel high pressure cylindrical cells. The cells were immersed into a reservoir containing synthetic groundwater and maintained immersed until saturation was reached. Then the tracer was added to the solution. Since the cells were confined by sintered discs, placed on each side of the sample with an open cap, the tracer could enter the clay from both sides. The variation of tracer concentration in the immersion bath was monitored periodically. At the end of the experiment the clay plugs were sliced following a standard method (Hume, 1993) and the concentration profile along the bentonite was obtained.

The solution to the transport equation for a radionuclide in a porous medium in one dimension with the boundary conditions defined by the previous described experimental set-up and considering the cylinder as infinite is (Put and Henrion, 1992):

$$C_b(x,t) = A \exp(Bx + B^2Dt) \operatorname{erfc} \frac{x + 2BDt}{2\sqrt{Dt}} \quad (2)$$

where C_b is the concentration in the “bulk” of the porous material, C_0 is the initial concentration in the solution, x is the position coordinate, D is the diffusion coefficient, t is time, A is $\varepsilon R_f C_0$, and B is $\varepsilon R_f C_0 S / Q_0$, where Q_0 is the mass of radionuclide initially deposited, R_f is the retardation factor, S is the area of the clay plug, and ε is the diffusion accessible porosity.

The parameters that can be directly obtained using this equation are the apparent diffusion coefficient, D , and the product εR_f .

Eq. (2) is fitted to the experimental results by adjusting the model parameters A , B and Dt , and the fit is performed considering separately the data of the two halves of the cell. As can be observed, A and B are parameters which are strictly related and their ratio ($(A/B) = (Q_0/S)$) can be evaluated experimentally. If the experimental time is large enough to obtain a constant profile within the plug, the distribution coefficient for the compacted clay can be directly evaluated.

ID experiments were simulated with the numerical approximation, considering five different regions: the first inlet region, the first sinter, the clay plug, the second sinter and finally the second inlet region. The model sizes and finite element mesh are different from those of the TD experiments. The initial concentration in both inlet regions is equal to the initial tracer concentrations, in the sinters and the clay plugs, the initial concentration is equal to zero.

3. Results and discussion

3.1. TD experiments

Fig. 1a shows the typical evolution of the HTO concentration in the IN and OUT reservoirs: for HTO the sum of the concentrations in the two reservoirs is always a

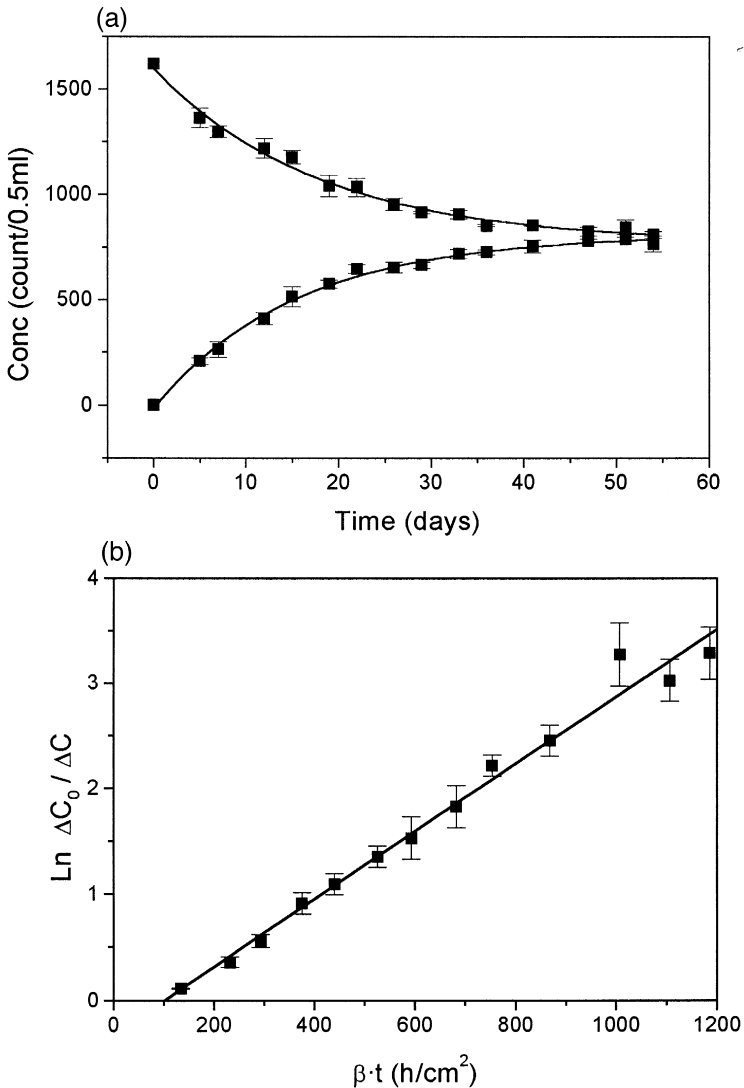


Fig. 1. (a) Typical HTO concentration evolution in both IN and OUT reservoirs observed during TD experiments. The continuous line corresponds to the best fit obtained with numerical methods. (b) Evaluation of the diffusion coefficient for HTO according to Eq. (1) from the experimental data plotted above.

constant, as expected to occur for a conservative element. After approximately two months, the equilibrium between the concentrations in the reservoirs is reached. Fig. 1b shows the representation of the HTO experimental data using Eq. (1). In the range of densities considered, the behaviour of the diffusion coefficient is linear with the dry density, decreasing when increasing the compaction degree, as shown in Fig. 2. This decrease can be related to the changes in the porous structure of the bentonite,

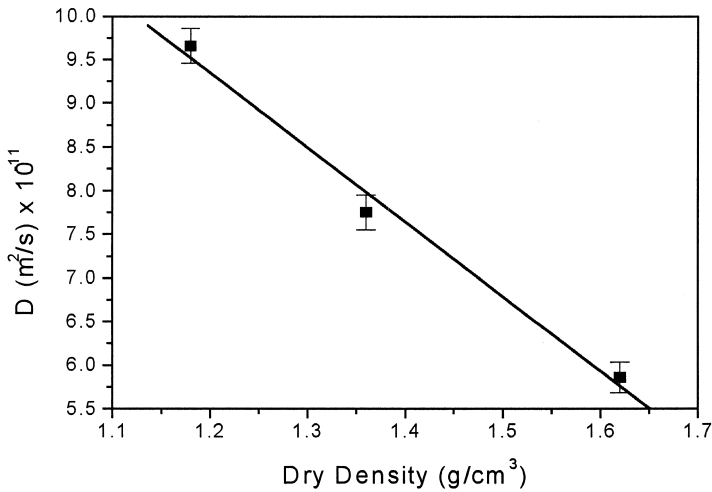


Fig. 2. HTO diffusion coefficient as a function of the dry density of the clay.

particularly the increase in the tortuosity (Sato et al., 1993). The linear relation found is the following: $D \text{ (m}^2/\text{s)} = (19.60 - 8.54\rho) \times 10^{-11}$. For a dry density of 1.62 g/cm^3 , an averaged value of $D = (5.7 \pm 0.3) \times 10^{-11} \text{ m}^2/\text{s}$ is obtained.

The use of Eq. (1) for the interpretation of the experimental results does not take into account the presence of the sinters, whose effect could be relevant specially for thick plugs and highly sorbing tracers (Yu and Neretnieks, 1997). These experiments were interpreted numerically in two stages. In the first one, in which sinters are not taken into account, estimated diffusion coefficients coincide with those obtained with Eq. (1). In the second stage, by considering the role of the sinters, values of approximately a factor 2 higher are obtained. In fact, for a dry density of 1.62 g/cm^3 , a value of $1.23 \times 10^{-10} \text{ m}^2/\text{s}$ was obtained.

In TD experiments with strontium, a significant decrease of the concentration (up to 0.22% of the initial concentration) was observed in the IN reservoir and no strontium was observed in the OUT reservoir, indicating that the element has been strongly retained onto bentonite. Fig. 3 shows the representation of data following Eq. (1). As can be observed, data cannot be fitted with a unique straight line. Two different slopes can be clearly seen and two different coefficients could be calculated. As it has been mentioned before, by applying this method, behaviours related to the “loading” of the radionuclide can be observed; strontium is in fact a sorbing species. Two steps describing the migration can be clearly distinguished: the first one, much faster, which is mainly influenced by sorption/loading processes and a second one, slower, which is most likely a diffusion-controlled process. Therefore, the coefficient obtained with the data in the second step is the one that really describes the diffusion process. The average value for strontium diffusion coefficient obtained with TD experiments, applying Eq. (1) is $(5.5 \pm 1.7) \times 10^{-12} \text{ m}^2/\text{s}$.

The mean diffusion coefficient obtained with numerical methods is $(6.06 \pm 0.75) \times 10^{-13} \text{ m}^2/\text{s}$ and the K_d value estimated is $695 \pm 138 \text{ ml/g}$. In this case, the diffusion

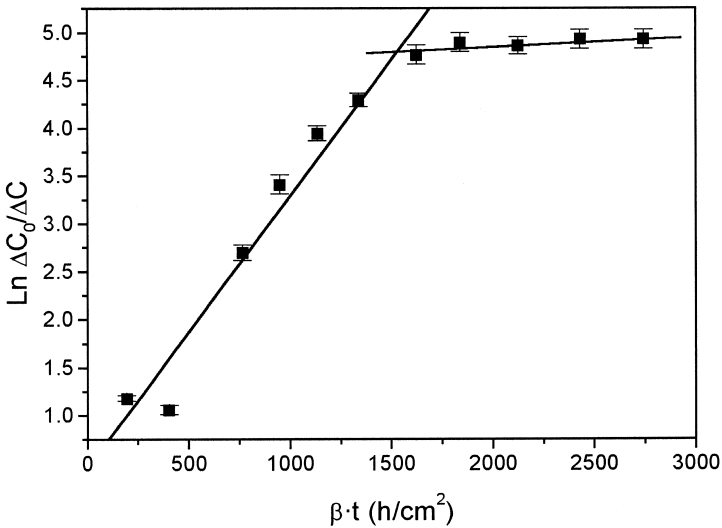


Fig. 3. Evaluation of the diffusion coefficient for strontium according to Eq. (1).

coefficient is one order of magnitude lower when the sinters are considered. These K_d and apparent diffusion coefficient results are in agreement with those proposed for strontium by Brandberg and Skagius (1991) (600–1300 ml/g) for batch sorption experiments and by Yu and Neretnieks (1997) (2.3×10^{-13} – 4.8×10^{-11} m²/s) for the apparent diffusion coefficient.

3.2. ID experiments

Fig. 4 shows a typical concentration profile obtained for cesium after slicing the clay plug at the end of the ID experiments. The continuous line on the experimental points corresponds to the best fit of the data obtained using the Eq. (2). As can be seen in the figure, concentration profiles are not completely symmetrical. The compaction of the clay is made by means of a hydraulic press and this method can produce a final density in the bottom of the plug slightly higher than that in the top. This fact is most likely responsible of the above-mentioned asymmetry. Since the mass of radionuclide initially deposited has not been distributed equally in both sides, Q_0 has been calculated by considering the mass actually entered by each side. The mean value for the diffusion coefficient, obtained from these experiments by fitting the concentration profiles to Eq. (2), is $(3.3 \pm 0.5) \times 10^{-13}$ m²/s for a density of 1.65 g/cm³.

By using the best fit value of εR_f and according to the retardation factor definition ($\varepsilon R_f = \varepsilon + \rho K_d$), K_d values were also obtained from the previous ID experiments. The porosity used for these calculations was 0.26, which is the value of the dynamic porosity of the FEBEX bentonite estimated by means of permeation experiments with HTO (García-Gutiérrez et al., 1999). In spite of the uncertainties of the porosity accessible for a specific radionuclide, it has to be taken into account that the εR_f values for cesium are

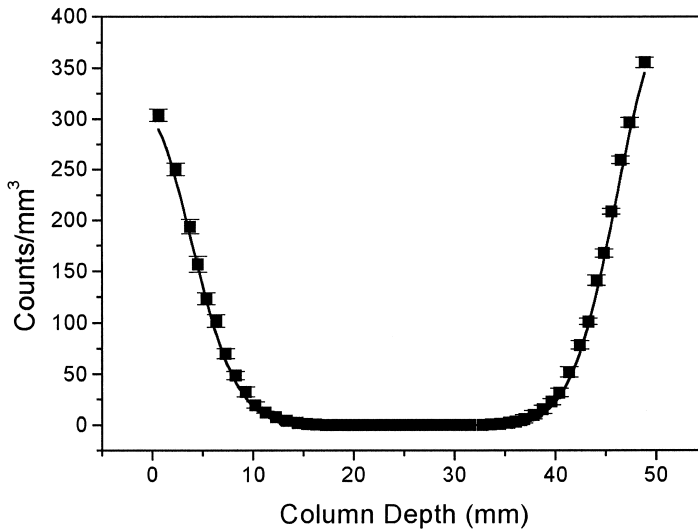


Fig. 4. Typical example of the profile concentration in the plug obtained for cesium after an ID experiment. The continuous line corresponds to the best fit obtained with Eq. (2). The experiment lasted 439 days.

quite high and an uncertainty in the porosity would produce negligible uncertainties in K_d . Therefore, for this element, K_d values estimated with this method are reliable. The calculated mean value is 823 ± 121 ml/g.

The diffusion coefficients obtained with numerical methods is $(2.64 \pm 0.70) \times 10^{-13}$ m²/s and the estimated K_d value is 919 ± 11 ml/g. The very good agreement between analytical and numerical methods indicates that the effect of the sinters vanishes, even for high sorbing species as cesium, if the clay plug is much thicker than the sinters.

The diffusion coefficient obtained in this work for cesium are in very good agreement with those obtained by Choi et al. (1992) for Ca-bentonite (6.7×10^{-13} and 1.7×10^{-13} m²/s for bentonite at density of 1.52 and 1.78 g/cm³, respectively).

In ID experiments with Se, the concentration in the reservoir was slowly decreasing with time (after 350 days a decreasing of approximately 15% was observed). Fig. 5 shows the typical profile concentration of Se in the plug. In all tests performed with selenium, it was impossible to obtain a good fit using Eq. (2) with a unique set of parameters. In Fig. 5, it can be seen that the experimental curve presents two slopes and we are able to fit the first or the second stretch with different sets of parameters but not all the points simultaneously. The fact that the diffusant may undergo chemical reactions during diffusion could not be taken into account by this model. Selenium could be present in different oxidation states and, in the chemical environment of bentonite, different complexes with different properties and different diffusion coefficients can be formed. Our results indicate that two different fractions exist: a faster moving fraction and another fraction presenting higher retention in bentonite than the first one. The difference in the diffusion coefficients for the two fractions is approximately one order of magnitude, $(6.25 \pm 2.94) \times 10^{-14}$ to $(1.56 \pm 0.34) \times 10^{-13}$ m²/s, respectively. As

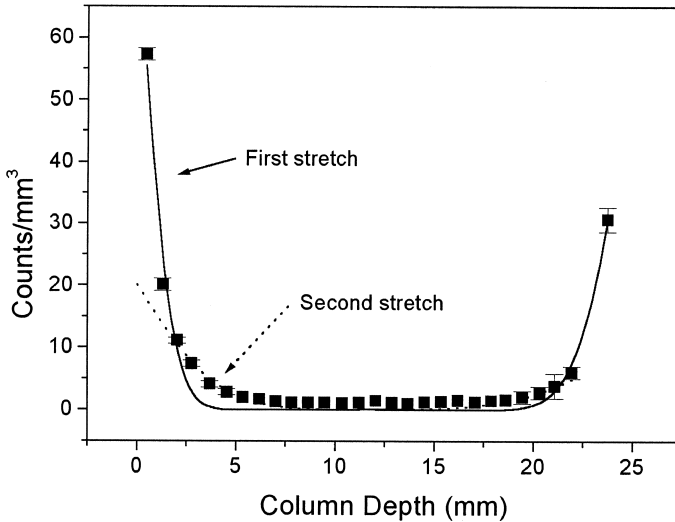


Fig. 5. Typical example of the profile concentration in the plug obtained for selenium after an ID experiment. The continuous and dotted lines correspond to the best fit obtained with Eq. (2) for the first and second stretch of the curve, respectively. Two different diffusion coefficients result from these fits. The experiment lasted 446 days.

for cesium, estimated K_d s were approximately 11 and 3 ml/g for the high and low sorbing selenium fraction, respectively.

The diffusion coefficient for selenium obtained from numerical methods is $(2.81 \pm 0.58) \times 10^{-14}$ m²/s. The fit was performed considering the first part of the profile, and also in this case a good fit of the second part was not obtained with the same diffusion coefficient. The value is in agreement with that obtained for the same part of the curve using the analytical solution. The K_d value obtained with from fit is 1.94 ± 0.07 ml/g.

Brandberg and Skagius (1991) proposed a K_d value of selenium in compacted bentonite of 1–2 ml/g at pH between 8.1 and 9.1. Oscarson et al. (1984) reported a K_d value of 3 ml/g at a pH of 7.0. Yu and Neretnieks (1997) proposed a realistic K_d value of 3.0 ml/g. The K_d values obtained in this work are consistent with all those works.

4. Conclusions

K_d and diffusion coefficients for HTO, Se, Sr and Cs in compacted FEBEX bentonite were evaluated by means of different experimental techniques and different methods of analysis of experimental results. It has been observed that among the elements studied, cesium presents the highest adsorption values. Strontium shows high K_d values and selenium lower values. ID experiments with selenium could not be fitted with a unique set of parameters, suggesting that selenium could be present in different oxidation states or could form complexes within bentonite with different diffusion coefficients that differ an order of magnitude. Anion exclusion effects can be also responsible for these effects.

In all the cases, K_d values evaluated in compacted bentonite are at least one order of magnitude lower than those evaluated in batch experiments (Yu and Neretnieks, 1997).

TD experiments performed with the method proposed by Wolfrum et al. (1988) have resulted in a very good method for the determination of diffusion coefficients with simple experimental conditions. However, TD experiments, which are generally performed in thin clay plugs, are suitable only for low sorbing species.

When the clay plug is much thicker than the sinters, the contribution of filter resistance is negligible and a very good agreement between numerical and analytical solution exists.

The main advantage of the numerical treatment consists in the possibility to account easily for the presence of sinters as well as time-varying boundary conditions. In addition, the use of numerical methods allowed to obtain in all cases diffusion and distribution coefficients simultaneously.

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