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Overview of laboratory methods employed for obtaining diffusion coefficients in FEBEX compacted bentonite

Descripción de los métodos de laboratorio empleados para obtener coeficientes de difusión en bentonita compactada FEBEX

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Abstract

This paper gives an overview of the main experimental methodologies usually applied to obtain diffusion parameters in compacted clays and of the analytical solutions that can be used according to the experimental configuration, initial and boundary conditions.

Each experimental method shows different advantages/limitations according to the type of element to be studied: neutral, anionic or cationic. Neutral species, such as tritium (HTO), do not interact with the solid and use all the porosity for diffusive transport; anionic elements, such as chloride, do not adsorb either but suffer anionic exclusion. Diffusion of cationic elements is retarded by sorption.

In order to describe how determine the diffusion parameters (apparent, D_a, and effective, D_e, diffusion coefficients and accessible porosity) examples of diffusion experiments of several radionuclides in the Spanish FEBEX bentonite will be used.

Apparent diffusion coefficients were obtained for HTO, chloride, iodide, sulphate, caesium, uranium, strontium, selenium, rhenium and europium. Effective diffusion coefficients were determined for HTO, chloride, iodide, sulphate, caesium, uranium, strontium, selenium, technetium, sodium and calcium. The accessible porosity was determined for HTO, chloride, iodide and sulphate.

In particular, the diffusion behaviour of HTO and Cl⁻ was studied at different bentonite dry densities. Both apparent and effective diffusion coefficient showed an exponential decrease when the dry density increased, more pronounced in the case of Cl⁻. The accessible porosity for HTO was found to be identical to the total porosity. For chloride (and other anions) only a very small fraction of the total porosity is accessible for diffusion transport at the density used for compacted clay in a repository.

A summary of all the results obtained with this clay will be given in the paper.

Keywords: FEBEX bentonite, effective and apparent diffusion coefficient; accessible porosity; laboratory methods; radionuclides.

Resumen

Este trabajo describe las principales metodologías empleadas para obtener parámetros de difusión en arcillas compactadas, así como las soluciones analíticas que pueden usarse dependiendo de la configuración experimental y de las condiciones iniciales y de

contorno.

Cada método tiene diferentes ventajas y limitaciones, en función del tipo de elemento estudiado: neutro, aniónico o catiónico. Las especies neutras, como el tritio (HTO), no interactúan con el sólido y usan toda la porosidad para el transporte difusivo; los elementos aniónicos, como el cloro, tampoco se adsorben, pero sufren exclusión aniónica. La difusión de los elementos catiónicos se ve retardada por la existencia de sorción.

Para describir como determinar los parámetros de difusión (coeficientes de difusión aparente, D_a, efectivo, D_e, y porosidad accesible) se utilizan numerosos ejemplos de ensayos de difusión realizados con la bentonita española FEBEX.

Se obtuvieron el coeficiente de difusión aparente del tritio, cloruro, yoduro, sulfato, cesio, uranio, estroncio, selenio, renio y europio. Se determinó el coeficiente de difusión efectivo del tritio, cloruro, yoduro, sulfato, cesio, uranio, estroncio, selenio, tecnecio, sodio y calcio. Asimismo, se obtuvo la porosidad accesible para el tritio, cloruro, yoduro y sulfato.

En particular, el comportamiento frente a la difusión del HTO y Cl⁻, se estudió en función de la densidad seca de la bentonita. Tanto el coeficiente de difusión efectivo como el aparente muestran un descenso exponencial al aumentar la densidad seca, más pronunciado en el caso del Cl⁻. Se encontró, que la porosidad accesible para el HTO es igual a la porosidad total. En el caso del cloruro (y otros aniones) sólo una muy pequeña parte de la porosidad total, a la densidad de compactación utilizada para un almacenamiento, es accesible al transporte por difusión.

En este trabajo se presenta un resumen de todos los resultados experimentales obtenidos con la bentonita FEBEX.

1. Introduction

Chemical transport by diffusion plays an important role in many geologic processes and diffusion coefficients can be used in practice for the design and evaluation of waste containment barriers (Shackelford, 1991). In many designs of high-level radioactive waste (HLRW) repository, compacted bentonite is considered as an engineered barrier. Therefore, the determination and the understanding of the diffusion transport in compacted bentonite is a very important issue for the analysis and consideration of the many processes that may affect safety of the underground disposal of nuclear waste. For the performance assessment calculations of a repository, apparent and effective diffusion coefficients of relevant radionuclides in the bentonite are necessary.

Bentonite is a swelling clay due to its content of the smectite clay mineral montmorillonite. This clay has a very low permeability and high sorption capability for many solutes. Since, at repository conditions, the hydraulic gradient will be very low, and repositories are designed to be hosted by impermeable rock formations, the transport of radionuclides through the compacted bentonite is a diffusion-controlled process retarded by sorption. Diffusive transport of radionuclides in porous media is a complex process affected by many parameters, such as the properties of the diffusing species, the properties of the solid itself (pore structure, degree of compaction, adsorption properties, dry density), the geochemistry of the system (mainly pore water chemistry) and the temperature (Kozaki *et al.*, 2001).

In compacted clays, electrostatic forces between the negatively charged clay surfaces and the anions affect transport of anionic species, and generally, this interaction results in a smaller volume of pore water available for anion transport, a phenomenon called anionic exclusion (Muurinen and Lehikoinen, 1995). Thus, an additional important parameter for describing the transport of radionuclides is the accessible porosity, which is often difficult to determine, especially at high clay density, for anions. The term "accessible porosity" is used to denote the proportion of the total volume of a saturated porous material that is available for diffusion.

The aim of this work is to describe different possible experimental methods to determine the main parameter controlling diffusive transport in bentonite and to discuss the main advantage and limitations of each one. A summary of the experimental diffusion data obtained with the Spanish bentonite clay, for many radionuclides, will be illustrated.

2. Diffusion theory

Diffusion is the process by which atomic and molecular size particles move from regions of high concentration to regions of lower concentration. Diffusion describes mass transport due to the random motion of molecules and atoms, known as Brownian motion. The mass or particle flux F [ML⁻²T⁻¹] per unit cross-sectional area is directly proportional to the concentration gradient and, for one-dimensional system, is expressed as:

$$F = -D\frac{\partial C}{\partial x} \tag{1}$$

Equation (1) is known as Fick's 1ˢᵗ law. The diffusion coefficient D [L²T⁻¹] measures the rate at which the molecules spread and is the proportionality constant between concentration gradient and flux. C denotes, under water

saturation conditions, the solute concentration in the pore water [ML^{-3}] that depends on time t and distance x. Conservation of mass leads to Fick's 2nd law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (2)$$

Solute diffusion in porous media, such as compacted clay, differs from diffusion process in free water or ideal solutions. Diffusion is affected by the length of the diffusion path, tortuosity (τ), the irregular form of the pores, constrictivity (δ), and possibly by the pore size. These terms are purely geometric, but satisfactory methods for determining them independently, do not exist. The definition of a *pore* diffusion coefficient partially overcomes this problem. The *pore* diffusion coefficient, D_p, is related to the diffusion coefficient in free water, D_w, by:

$$D_p = \frac{\delta}{\tau^2} D_w \qquad (3)$$

The simple pore diffusion model is equivalent to a model in which a channel through the porous media exists, the cross-sectional area of pipes per unit area being porosity. Actually the situation is more complex in porous systems where dead-end and blind pores or different levels of porosity exist.

In porous media, the volume available for diffusion is given by the pores that are connected and contribute to the transport of the dissolved species, from one side to the other of the clay sample.

The *effective* diffusion coefficient, D_e, takes account of the smaller cross-sectional area available for diffusion in porous media and is defined by:

$$D_e = \varepsilon \cdot D_p \qquad (4)$$

where ε is the porosity or water content in a water saturated medium, which can be experimentally obtained, for instance, by means of saturation experiments.

Therefore, under steady state conditions the mass flux given by equation (1) in porous media is defined by:

$$\qquad (5)$$

where F is expressed in units of mass or moles per total cross-section area of porous medium per time, D_e substitutes D in the expression of second Fick's law, equation (2):

$$\varepsilon \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \qquad (6)$$

where ε is assumed not to change with time and the medium is assumed to be homogeneous (constant D_e).

In the case of sorbing elements, the attainment of the steady state can be very time consuming. However, an apparent diffusion coefficient, D_a, can be calculated from the transient diffusion through the sample. The mass of solute tracer, M, per a representative volume of saturated porous medium, $(\Delta x)^3$, is given by the sum of the solute concentration in the pore water, C, and the sorbed concentration per mass of solid phase, S:

$$M = \varepsilon \cdot C (\Delta x)^3 + \rho_d \cdot S (\Delta x)^3 \qquad (7)$$

where ρ_d is the bulk density of the dry material. When sorption is present, any change in solution concentration is accompanied by a change in the sorbed concentration. Therefore, taking into account the equation (7), the second Fick´s law, equation (6), is written now as:

$$\varepsilon \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \rho_d \frac{\partial S}{\partial t} \qquad (8)$$

where both ε and ρ_d are assumed not to change with time.

If instantaneous lineal sorption is considered, the sorption isotherm can be described by the simple relation $S = K_d \cdot C$, where S is the tracer concentration on the solid phase; C, the tracer concentration in the liquid phase; and K_d, the distribution coefficient. Equation (8) can be rewritten as:

$$\left(\varepsilon + \rho_d \cdot K_d \right) \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \qquad (9)$$

and the second Fick´s law in the case of sorbing species can be written similarly as equation (2) and (6) for the one-dimensional case as:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \qquad (10)$$

where the relation between D_e and D_a is:

$$D_a = \frac{D_e}{\varepsilon + \rho_d \cdot K_d} = \frac{D_e}{\alpha} \qquad (11)$$

The term $\varepsilon + \rho_d \cdot K_d$ is a dimensionless parameter also known as the capacity factor, α, of the porous medium or rock capacity factor. For conservative solutes, $K_d = 0$, so that the capacity factor is equal to the porosity.

The retardation factor, R_f, is defined by:

$$R_f = 1 + \frac{\rho_d}{\varepsilon} K_d \qquad (12)$$

Equation (11) can be written as:

$$D_a = \frac{D_e}{\varepsilon \cdot R_f} = \frac{D_p}{R_f} \qquad (13)$$

Thus, D_a takes explicitly into account the retardation of the solute due to the interactions with the porous material.

So far, it is assumed that porosity ε is totally available for diffusion and that ε is a material property independent of the species of the tracer being considered. Normally, this porosity is taken equal to the porosity of the media determined from the water content. However, the effective porosity available for diffusion transport can be smaller than the value determined from the water content, since some pores may not be accessible or not contribute to the solute transport such as dead end or blind pores. Furthermore, processes such as anion exclusion from the vicinity of the negatively charged clay surface may also reduce the effective porosity (Lever *et al.*, 1985; Rowe *et al.*, 1988).

The total porosity of the sample, ε, is the ratio of the pore volume to the total volume of a representative sample of the medium. For a medium with a dry density, ρ_d, and solid density, ρ_s, the total porosity can be obtained by:

$$\varepsilon = 1 - \frac{\rho_d}{\rho_s} \tag{14}$$

The accessible porosity represents the fraction of the total porosity available for solute transport. Therefore, for each ion an "accessible porosity" should be considered.

For conservative elements, the capacity factor is equal to the porosity, and equation (11) shows the relationship between D_e, D_a, and the porosity. If two parameters are measured, the third one can be calculated, as has been done in this article for Cl⁻, I⁻ and $SO_4^=$ (D_e and the accessible porosity were measured and D_a was calculated). When all three parameters can be measured and they satisfy equation (11), the consistency of the values obtained is proved, as has been done in this article for HTO.

3. Materials

FEBEX bentonite comes from the Cortijo de Archidona (Almería, Spain). This clay has a smectite content greater than 90% (93±2%), with quartz (2± 1%), plagioclase (3± 1%), cristobalite (2±1%), potassic feldspar, calcite, and trydimite as accessory minerals. The specific weight of the FEBEX bentonite is 2.7 g/cm³. An exhaustive description of this clay can be found elsewhere (Huertas *et al*, 2000; Villar *et al.*, this volume). Bentonite cylindrical plugs were compacted at different dry densities (from 1.0 to 1.7 g/cm³) with special emphasis on the density of 1.65 g/cm³, because this is the density considered in the Spanish reference concept for radioactive waste repositories

in granite and clay. The plugs, with a diameter of 3.8 or 5 cm, were located in a stainless steel high-pressure cell and sandwiched between sintered steel filters.

In all the experiments, the bentonite samples were saturated with water. Complete water saturation of the samples was verified by a final, stable weight at the end of the experiment.

Tritiated water (HTO) was used as conservative tracer because it is expected to be representative of all the chemical elements that do not show retention in the solid phase. Cl⁻, SO_4^{2-} and I⁻ were used as anionic species and a large number of radionuclides from low to highly sorbing were used.

The tracers were mainly radioactive, and were measured by liquid scintillation counting for beta or alfa-beta emitters (HTO, ³⁶Cl⁻, ³⁵$SO_4^=$, ²³³U(VI), ⁹⁹Tc(VII) and ⁴⁵Ca(II)) using a TR-2700 Packard apparatus, and for gamma emitters (¹³⁷Cs(I), ¹⁵²Eu(III), ²²Na(I), ⁷⁵Se(IV), ⁸⁵Sr(II)) using a Packard autogamma Cobra II apparatus. In the case of Re, and I, stable isotopes were used and measured by means ICP-MS or using a selective electrode, respectively. When it was necessary to extract the tracer from the clay (e.g. in the case of ³⁶Cl⁻), the plug was sliced and the solid of each slice was re-suspended in water and the tracer activity measured after centrifugation of the supernatant.

4. Experimental methods and analytical approaches.

4.1. Diffusion coefficients

In general, the methods used to measure the diffusion coefficients (both effective and apparent) of chemical species can be classified into two categories, steady state and transient. Transient methods are experimentally easier to carry out whereas steady-state usually require a much larger experimental time (Flury and Gimmi, 2002; Shackelford, 1991). The description of each experimental method is accompanied by an example of experimental results obtained with the FEBEX clay.

4.1.1. Through-Diffusion with constant concentration in the reservoirs

A classical method for measuring diffusion coefficient is the Through-Diffusion technique, TD. In this method the sample is located in between two reservoirs, "in" and "out" reservoirs, where the solution is continuously stirred. After water saturation of the bentonite sample, the in-reservoir is spiked with the tracer. The concentrations in both reservoirs are kept constant such that steady-state diffusion across the sample is achieved. When steady
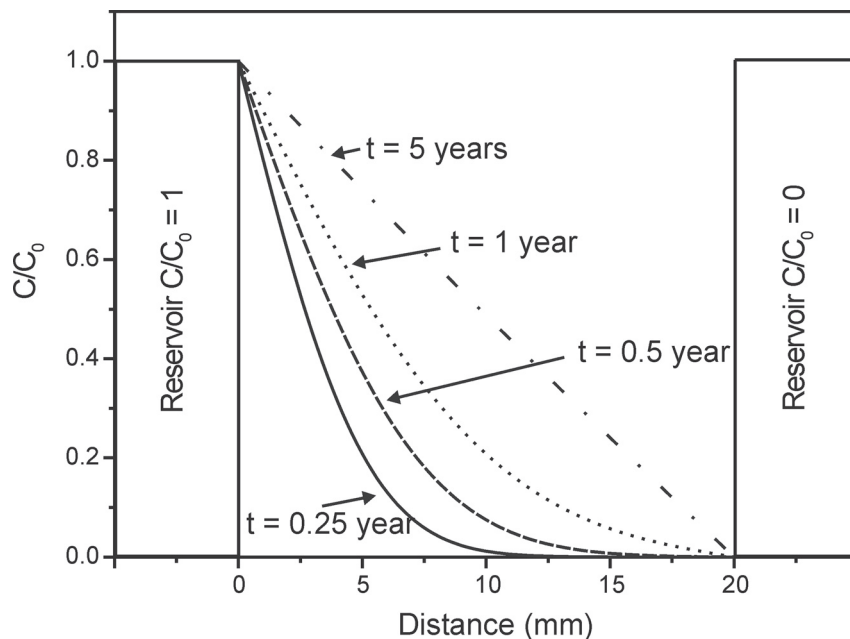
Fig. 1.- Diffusion profile into the clay plug. When the steady-state condition is reached the concentration profile becomes a straight line.

Fig. 1.- Perfil de difusión dentro de la pastilla de arcilla. El perfil se hace una línea recta cuando se alcanza el régimen estacionario.

state is reached, the diffusive flux across the sample is constant. Different approximations can be used to maintain the constant concentration gradient: spiking additional tracer in the in-reservoir, if it is necessary, or using large volumes to minimise the concentration decrease; carrying out frequent sampling in the out-reservoir to maintain the concentration near to zero or to use small reservoir and changing them periodically. In our laboratory we usually use a configuration with a large (1 L) in-reservoir and a very small (20 mL) out-reservoir, which is changed periodically.

The initial and boundary conditions for a bentonite plug of thickness d [L], which is initially tracer free, and where the in-reservoir has a constant concentration C_0 and the out is kept "quasi" zero, are:

$C(x > 0, t = 0) = 0$
$C(x = 0, t > 0) = C_0$
$C(x = d, t > 0) = 0$

The concentration profile, at time t, in the plug is given by (Crank, 1975):

$$\frac{C}{C_0} = 1 - \frac{x}{d} - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin\left[\frac{n\pi x}{d}\right]\exp\left[\frac{-n^2\pi^2 D_a t}{d^2}\right] \quad (15)$$

Figure 1 shows the concentration profiles of a diffusing tracer with $D_a = 1\cdot10^{-12}$ m²/s through a 2 cm-thick sample and unit cross-sectional area, at different times. After a certain time (5 years in the figure), when steady-state conditions are reached, the concentration profile becomes a straight line.

The expression of the cumulative mass of tracer (M), that has passed to out-reservoir, through a cross-sectional area A, as a function of the time is (Crank, 1975; Bourke *et al.*, 1993):

$$M = C_0\cdot\alpha\cdot d\cdot A\left(\frac{D_a t}{d^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left[\frac{-n^2\pi^2 D_a t}{d^2}\right]\right) \quad (16)$$

For long time periods, the series expansion in equation (16) vanishes because the exponential term tends to zero and a linear relationship is obtained between M and t. The equation, expressed in terms of D_a and D_e (according with his relations) becomes:

$$M = C_0\cdot\alpha\cdot d\cdot A\left(\frac{D_a t}{d^2} - \frac{1}{6}\right) = C_0\cdot A\left(D_e\frac{t}{d} - \frac{\alpha\cdot d}{6}\right) \quad (17)$$

Figure 2a shows the normalized cumulative mass for equation (16), clearly showing a transient region, and the long-term approximation (dashed line) steady-state regime, from equation (17). The figure for equations (16) and (17) correspond to $D_a = 1\cdot10^{-12}$ m²/s through a sample of 1 cm of thickness and unit cross-sectional area.

The effective diffusion coefficient can be calculated from the slope of the straight line fitting the long-term behaviour of M. The intercept of equation (17) with the time axis is commonly denoted as time-lag (t_e):

$$t_e = \frac{d^2\alpha}{6\cdot D_e} \quad (18)$$

Figure 2b shows the cumulative mass *vs.* time of experimental points obtained in the FEBEX bentonite using
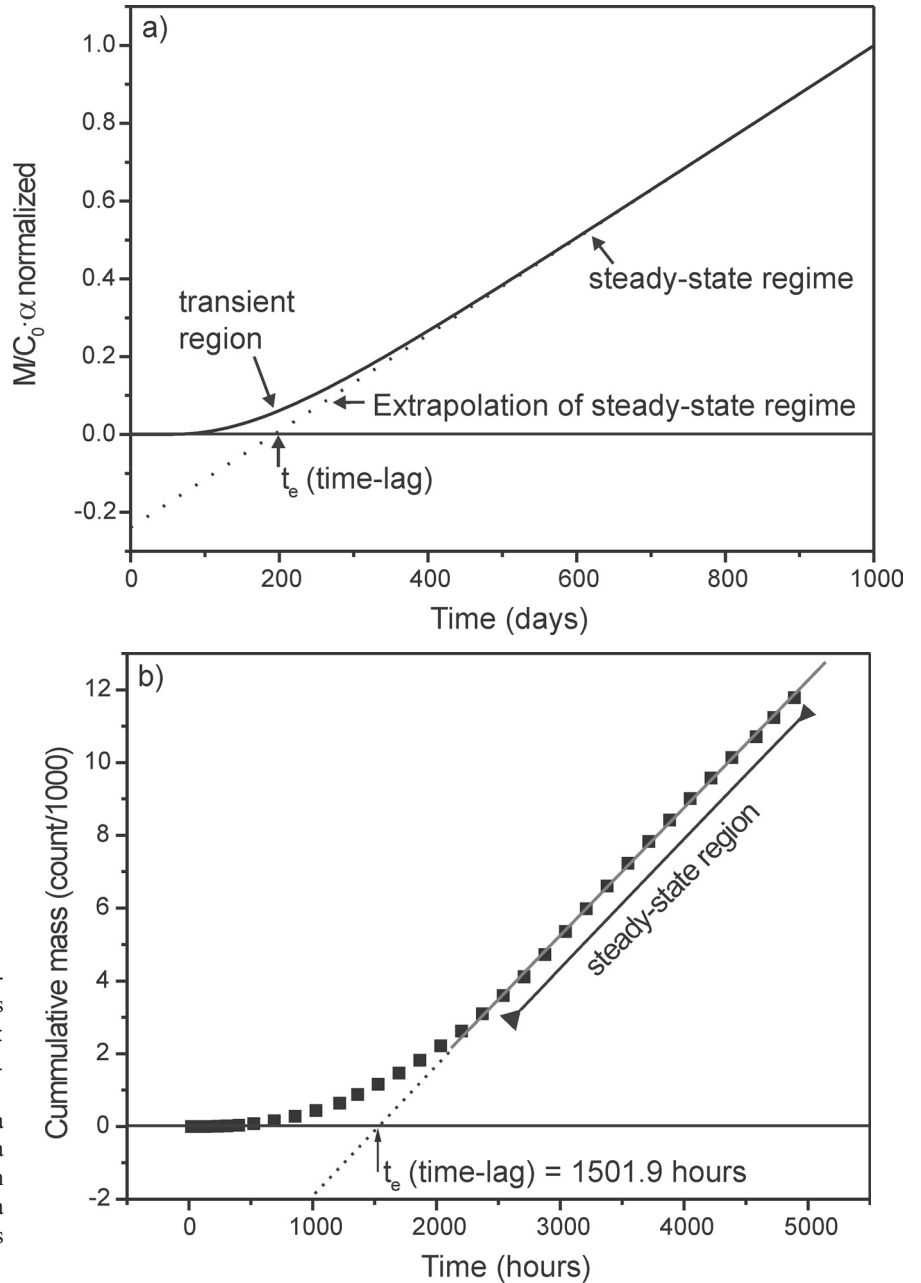
Fig. 2.- a) Normalized cumulative mass obtained in the outlet reservoir. Continuous line: general case, equation (17). Dotted line: approximation for long times, equation (18). b) Experimental results obtained using $^{36}Cl^-$.

Fig. 2.- a) Masa acumulada normalizada obtenida en el depósito de salida. La línea continua representa el caso general, ecuación (17); la línea de puntos la aproximación para tiempos largos, ecuación (18). b) resultados experimentales obtenidos utilizando $^{36}Cl^-$.

$^{36}Cl^-$ as tracer. From the steady-state region we obtained the effective diffusion coefficient. The time-lag value is also shown.

The capacity factor (that for conservative elements is equal to accessible porosity), can be calculated from the time-lag value.

The advantage of the steady-state method is that D_e of reactive tracers can be measured without knowing the R_f value. But the time necessary to reach the steady-state regime can be very long if the porous medium retards the tracer. The time required to establish steady-state conditions increases with sample thickness.

Keeping the concentration gradient constant is difficult, but small variations in the reservoirs concentrations can

be permitted and the application of the analytical solution is still valid. From an experimental point of view, this condition is maintained if in the in-reservoir the concentration does not vary more than 5% from its nominal value during the experiment, and in the out-reservoir the concentration should not exceed 10% of the concentration of the in-reservoir.

4.1.2. Through-Diffusion with variable concentrations in the reservoirs

If the restrictions on the concentrations in both reservoirs could be eliminated, the diffusion experiments would be simplified. A different class of through-diffusion experiments can be done, in which, after an initial spike of trac-

er in one reservoir, concentrations are allowed to evolve in both reservoirs and are continuously monitored.

According to an evaluation of Fick's second law, Wolfrum *et al.*, (1988), proposed to estimate the effective diffusion coefficient, when the temporal evolution of the concentrations in both reservoir is allowed, from the following equation:

$$D_e = \frac{\ln\left[\Delta C_0 / \Delta C\right]}{\beta \cdot t} \qquad (19)$$

where ΔC_0 is the initial concentration difference between the two reservoirs; ΔC is the concentration difference at time t; β is A/d $(1/V_a + 1/V_i)$, where V_a and V_i are the volumes of the reservoirs; A is the cross-sectional area of the clay plug, and d is the thickness of the clay plug. Wolfrum's method is based on a non steady-state condition and the approximation is valid only for conservative tracers (Cormenzana *et al.*, 2003).

The evaluation of the diffusion coefficients includes sampling of both sides of the clay plug. Effective diffusion coefficient can be obtained by a linear regression of the experimental data representing $\ln[\Delta C_0 / \Delta C]$ vs. $\beta \cdot t$.

Moridis (1999), developed semi-analytical solutions under the condition of diffusion cell experiments, which involve finite liquid volumes and temporally variable concentrations in the inlet and outlet reservoirs.

Figure 3a shows typical concentration evolution of both reservoirs for three different diffusion coefficients (D, 2D and 5D). The upper curves correspond to the concentration evolution in the in-reservoir, and the lower curves correspond to concentration evolution in the out-reservoir. Figure 3b shows experimental results and the fits obtained with HTO in FEBEX bentonite compacted at two different dry densities.

4.1.3. In-Diffusion method

In-Diffusion experiments, ID, are the typical transient essays. In these experiments the cell with the bentonite plugs is immersed into a large volume of water. After water saturation of the samples, which is verified by a final weight at the end of the experiment the tracer is added to the reservoir, and it can enter through one or both sides of the clay plug. After a given time, the diffusion cell is disassembled, the bentonite plug cut into slices, and the activity in each slice measured to obtain a concentration profile in the bentonite plug. Experiments are usually designed so that the tracer cannot reach the closed extreme of the sample (or the middle point if both extremes are open) and the experiment could be treated as a one-dimensional problem of diffusion into a semi-infinite medium.

If the concentration in the reservoir remains practically constant during the experiment and the bentonite plug is long enough to be considerer a semi-infinite medium, the following initial and boundary condition can be considered:

$C(x > 0, t = 0) = 0$
$C(x = 0, t > 0) = C_0$
$C(x = \infty, t > 0) = 0$

The concentration profile within the plug can be fit by the following analytical solution (Crank, 1975):

$$\frac{C}{C_0} = erfc\left(\frac{x}{2\sqrt{D_a t}}\right) \qquad (20)$$

where C is the tracer concentration in the bentonite plug pore water, C_0 the constant concentration in the reservoir, D_a the apparent diffusion coefficient, x the distance, and t the diffusion time.

The mass of tracer per unit area which has diffused into the plug after a certain time is (Grathwohl, 1998):

$$M = 2 \cdot C_0 \cdot \alpha \sqrt{\frac{D_a \cdot t}{\pi}} \qquad (21)$$

Figure 4a shows the theoretical concentration profiles in the plug for $D_a = 1 \cdot 10^{-12}$ m²/s at different times. Figure 4b shows experimental results from FEBEX clay samples at different densities and their simulations. Comparison of the experimental profile and the theoretical profiles, for different D_a values, allows identifying the value of D_a, for which the fitting is the best.

Both Through-Diffusion and In-Diffusion techniques are not appropriate for strongly sorbing tracers. In Through-Diffusion experiments, the tracer is not able to pass from a reservoir to another, (at least in reasonable time). Furthermore, in both methods, the tracer can be sorbed on the experimental cells and on the filters before reaching the clay.

Thus, when the tracer is strongly sorbing, the best option is to introduce it directly in the compacted clay, avoiding the contact with anything but the bentonite. There are several internal-source diffusion configurations for which analytical solutions to interpret diffusion data exist (see sections 4.1.4, 4.1.5 and 4.1.6).

4.1.4. Instantaneous planar source

If a filter paper tagged with a highly soluble tracer is located between two saturated bentonite clay plugs, we can consider a thin source of tracer or a instantaneous planar diffusion source. In this configuration, the symmetrical diffusion profiles are determined at the end of the experiment after slicing the bentonite sample. This is the easiest method, above all when a radioactive tracer is used.
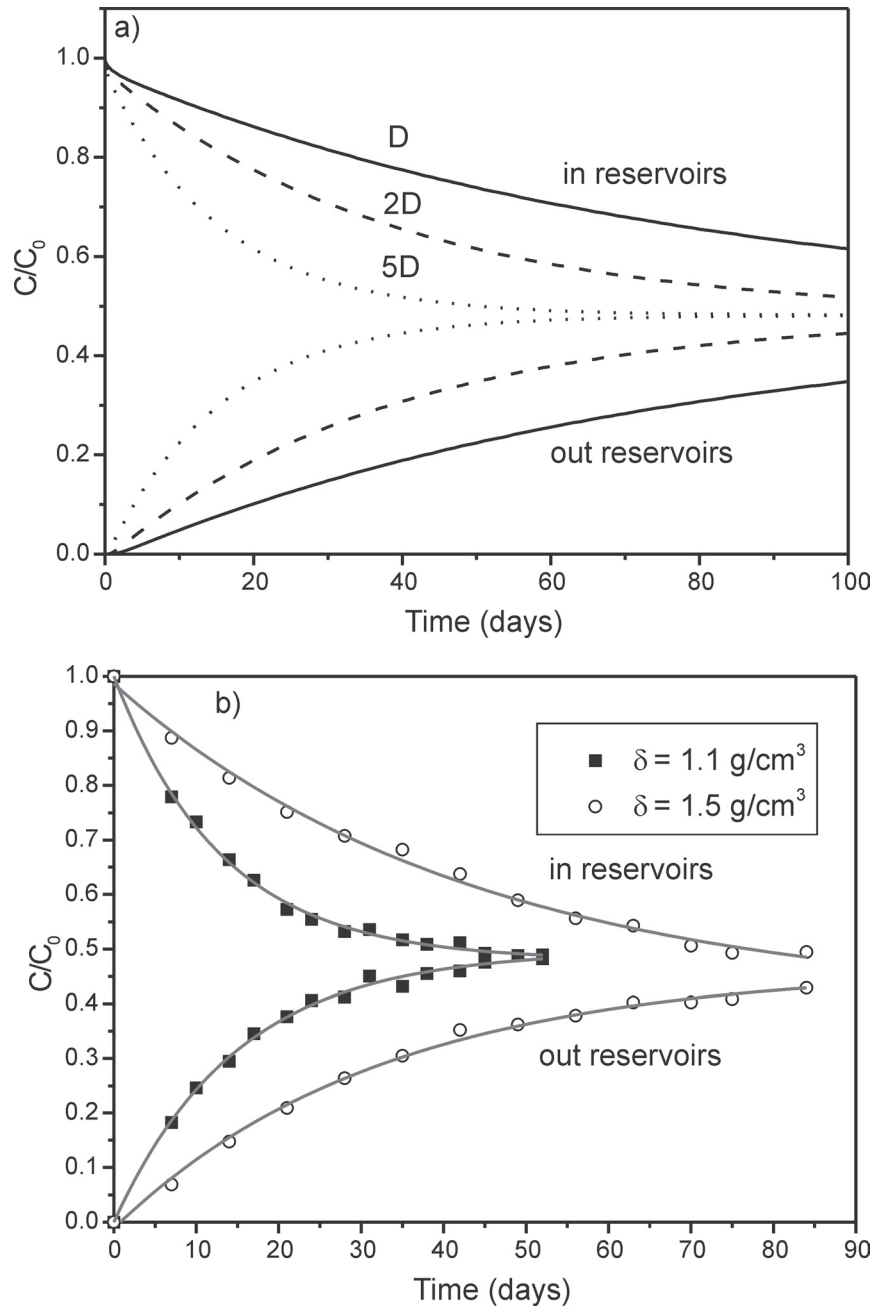
Fig. 3.- a) Concentration evolution for in- (upper curves) and out- (lower curves) reservoirs, obtained for three different diffusion coefficients. b) Experimental results and theoretical lines obtained for HTO at two different dry densities.

Fig. 3.- a) Evolución de las concentraciones en el depósito de entrada (curvas de la parte superior) y en el depósito de salida (curvas de la parte inferior), para tres coeficientes de difusión diferentes. b) Resultados experimentales y teóricos obtenidos utilizando HTO para dos densidades de compactación.

In this case, a mass of tracer M is injected uniformly across the cross-section of area A at point $x = 0$ at time $t = 0$. The initial width of the tracer is infinitesimally small, therefore we use the Dirac delta function, $\delta(x)$.

The initial and boundary conditions for this case are:

$C(x = 0, t = 0) = M/(\delta(x) \cdot A)$

$C(-\infty < x < \infty, t = 0) = 0$

The apparent diffusion coefficient for this arrangement is evaluated from the following analytical solution for unit cross-sectional area (Crank, 1975):

$$C(x,t) = \frac{M}{2\sqrt{\pi \cdot D_a t}} \exp\left(-\frac{x^2}{4D_a t}\right) \qquad (22)$$

By taking the logarithm of both sides of the previous equation, a linear expression is obtained, the slope of which gives the apparent diffusion coefficient. By the fit of the experimental concentration profile of C/M versus x is also possible to obtain the D_a. If the filter paper is situated in an end of the clay plug, the factor 2 in equation (22) disappears. For no unit cross-sectional area, equation (22) needs to be divided by it.

Figure 5a shows theoretical concentration profiles for $D_a = 1 \cdot 10^{-12}$ m²/s at different times for an instantaneous planar source. Figure 5b shows the experimental results obtained in FEBEX bentonite using europium as tracer, after two years of diffusion.
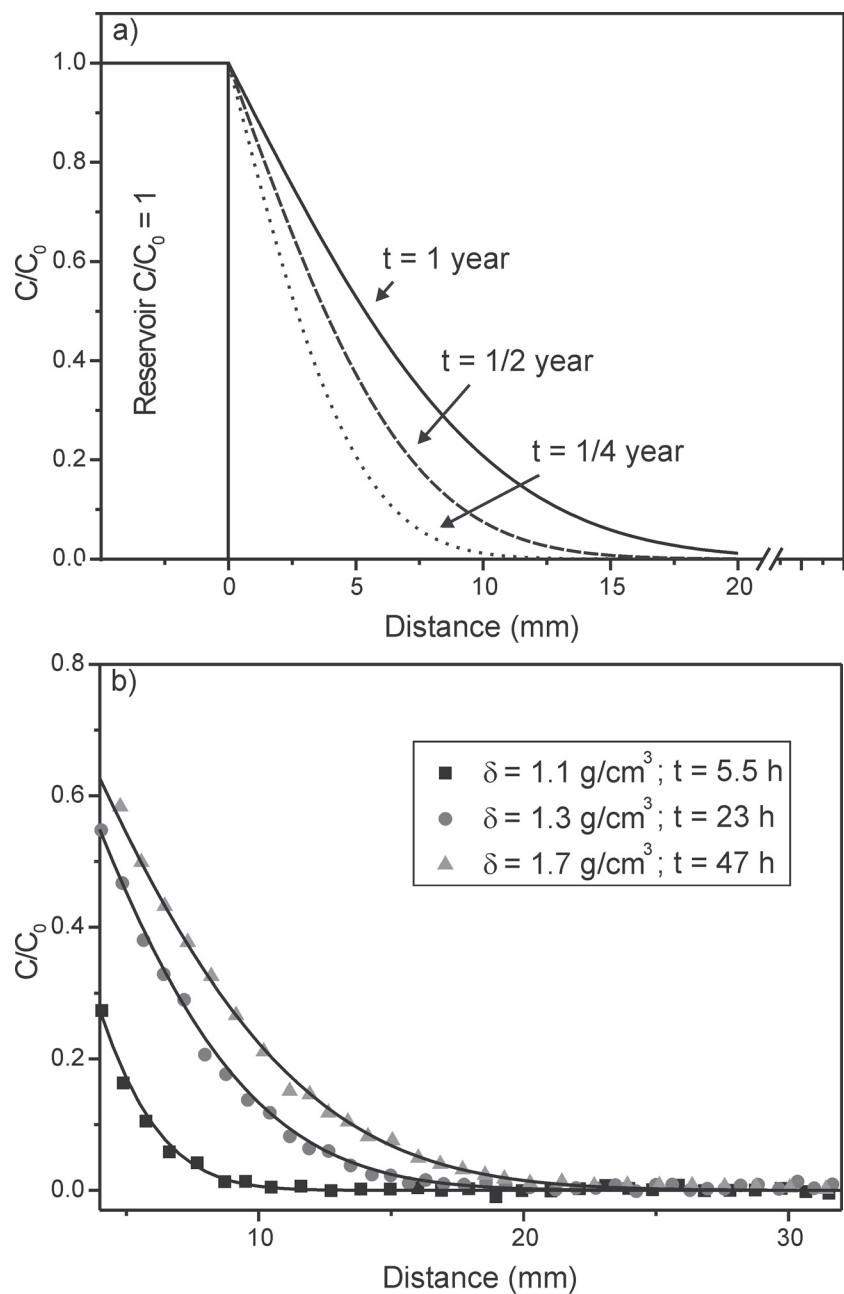
Fig. 4.- a) Concentration profiles into the clay plug at different times for a constant concentration source. b) Experimental results and theoretical lines obtained with HTO at three different dry densities.

Fig. 4.- a) Perfiles de concentración en la pastilla de arcilla en función del tiempo, para un depósito de concentración constante. b) Resultados experimentales y teóricos obtenidos utilizando HTO para tres densidades de compactación distintas.

4.1.5. Half-plugs method

Two half-plugs of clay, one tagged with tracer, are placed together to allow diffusion of tracer to occur from the tagged plug to the other one. The mass of solute in the tagged plug decreases as the solute diffuses into the untagged plug. As long as the concentration profile does not reach the ends of the plugs, the porous medium can be considered to be infinite and the following analytical solution is valid.

The initial and boundary conditions for this case are:

$C(x \leq 0, t = 0) = C_0;$ $C(x > 0, t = 0) = 0$

$C(x = -\infty, t > 0) = C_0$

$C(x = \infty, t > 0) = 0$

and the analytical solution is (Crank, 1975):

$$C = \frac{1}{2}C_0 \cdot erfc\left(\frac{x}{2\sqrt{D_a \cdot t}}\right) \qquad (23)$$

After an elapsed time, the clay plugs are sliced and the experimental concentration profile can be fitted to the theoretical profiles to obtain the diffusion coefficient. Measuring the total amount of tracer transferred from one plug to the other plug at a specified time the diffusion coefficient can be determined also. Figure 6a shows the theoretical concentration profiles for $D_a = 1 \cdot 10^{-12}$ m²/s at different times. Figure 6b shows experimental results obtained in the FEBEX bentonite at 1.65 g/cm³ dry density with HTO as tracer.
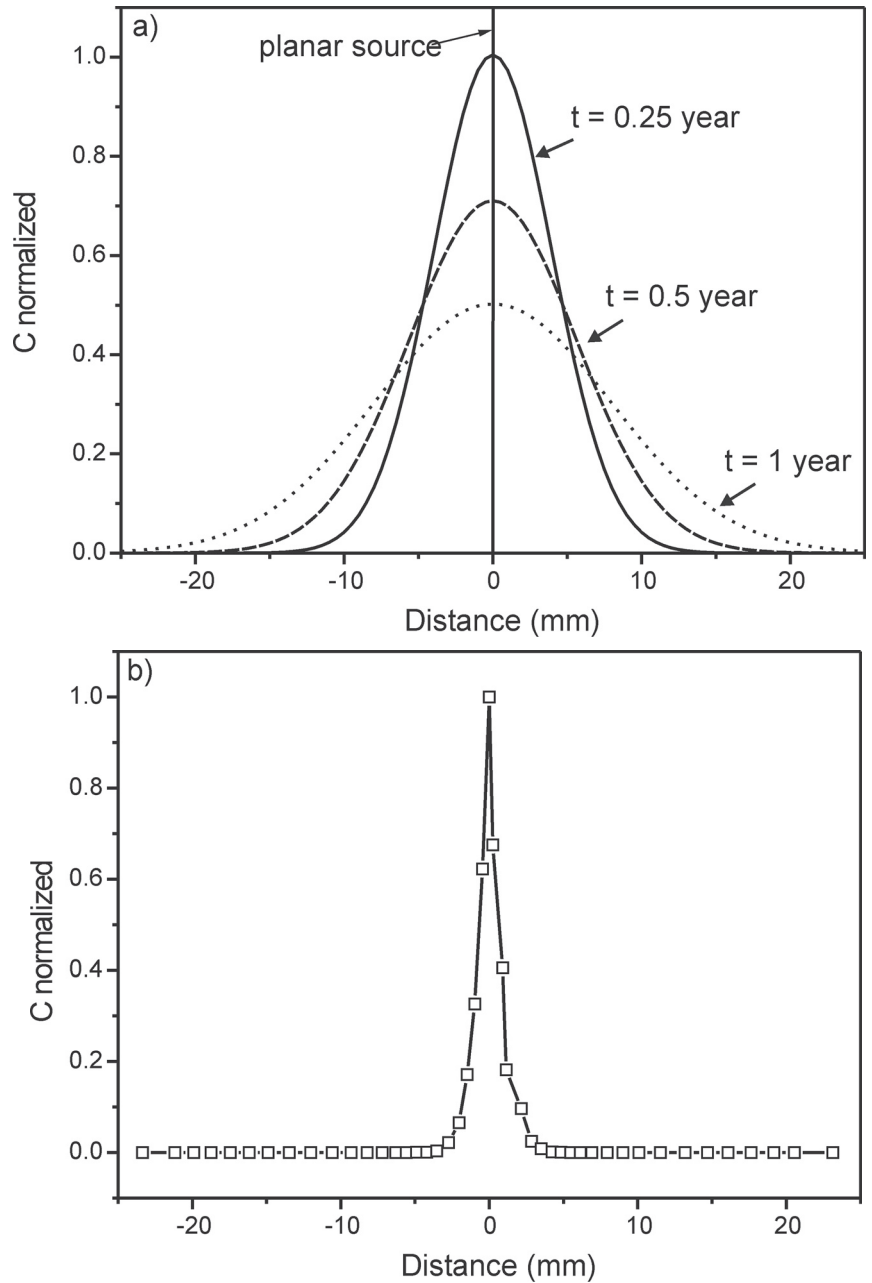
Fig. 5.- a) Theoretical concentration profile from a instantaneous planar source in a saturated one-dimensional porous medium at different times. b) Experimental results obtained using europium, after two years of experimental time.

Fig. 5.-a) Perfiles de concentración teóricos obtenidos para el caso de una fuente plana instantánea, situada en un medio poroso unidimensional saturado, en función del tiempo. b) Resultados experimentales obtenidos con europio, después de dos años de experimentación.

4.1.6. Thick source method

Another possible configuration is to introduce a bentonite plug tagged with the tracer between two untagged plugs (thick source). The mass of solute in the tagged plug decreases as the solute diffuses into the untagged plugs. As long as the concentration profile does not reach the end of the plugs, the porous medium can be considered to be infinite and the following analytical solution is valid.

The initial and boundary conditions for this new case are:

$C(x < -h, t = 0) = 0; \quad C(x > h, t = 0) = 0$

$C(-h \leq x \leq h, t = 0) = C_0$

$C(x = \pm\infty, t > 0) = 0$

and the analytical solution is (Crank, 1975):

$$C = \frac{1}{2}C_0 \cdot \left[erf\left(\frac{x+h}{2\sqrt{D_a \cdot t}}\right) - erf\left(\frac{x-h}{2\sqrt{D_a \cdot t}}\right) \right] \qquad (24)$$

Figure 7a shows theoretical concentration evolution for $D_a = 1 \cdot 10^{-12}$ m^2/s at different times for a thick plug of 1 cm ($h = 0.5$ cm). The peak position or maximum concentration decrease with time and can be calculated when $x = 0$ in equation (24). Figure 7b shows HTO experimental results using a thick plug of 1 cm of FEBEX bentonite compacted at 1.7 g/cm^3.

The thick source can result from the relatively short-time disintegration of a waste container in long-term
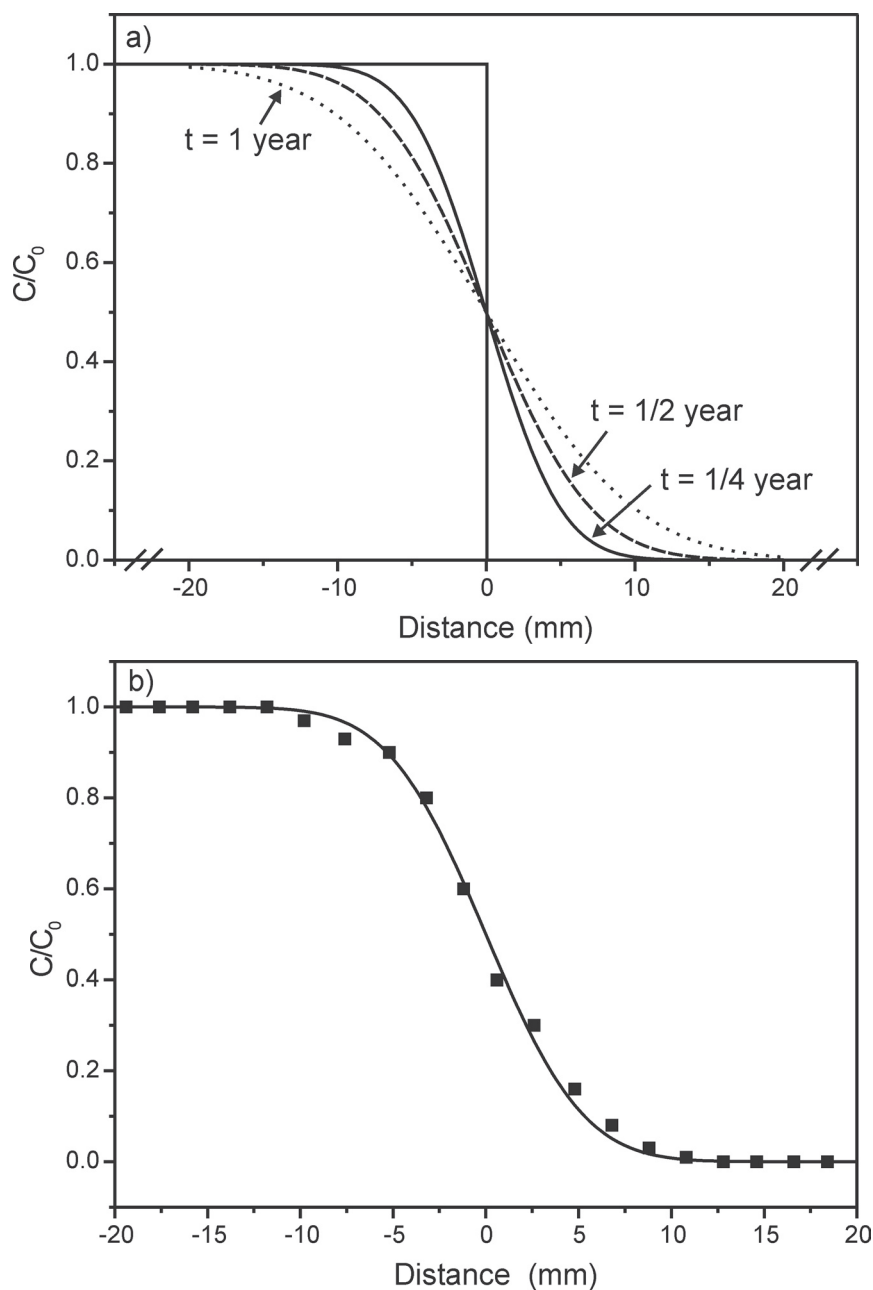
Fig. 6.- a) Concentration profiles in the spiked and unspiked half plugs for an infinite system at different times. b) Experimental results obtained with HTO at 1.65 g/cm³ dry density.

Fig. 6.-a) Perfiles de concentración en función del tiempo, en la pastilla dopada y sin dopar, considerando un medio infinito. b) Resultados experimentales obtenidos utilizando HTO a 1,65 g/cm³ de densidad.

storage, therefore it is a problem of practical importance, when we have a long-term leaching of a low solubility material.

Internal source diffusion experiments were designed for strongly sorbing elements, but it is worth mentioning that this configuration can be also successfully used for less sorbing or even conservative elements.

4.2. Accessible porosity

Accessible porosity can be measured by means of different methods. Saturation experiments allows determining directly the accessible porosity, but it is possible to estimate it, using indirect methods like the time-lag method, or comparing the values of the apparent and effective diffusion coefficients.

The methods explained in this section provide the accessible porosity for anionic and conservative species and the capacity factor for non-conservative species.

Saturation experiments are performed introducing the diffusion cell into a bath with tracer; in these experiments, a constant lineal concentration profile in the clay plug has to be obtained when tracer concentration equilibrium is reached. In order to ensure that the concentration profile into the plug is effectively constant, the concentration in the saturation solution is periodically monitored until a
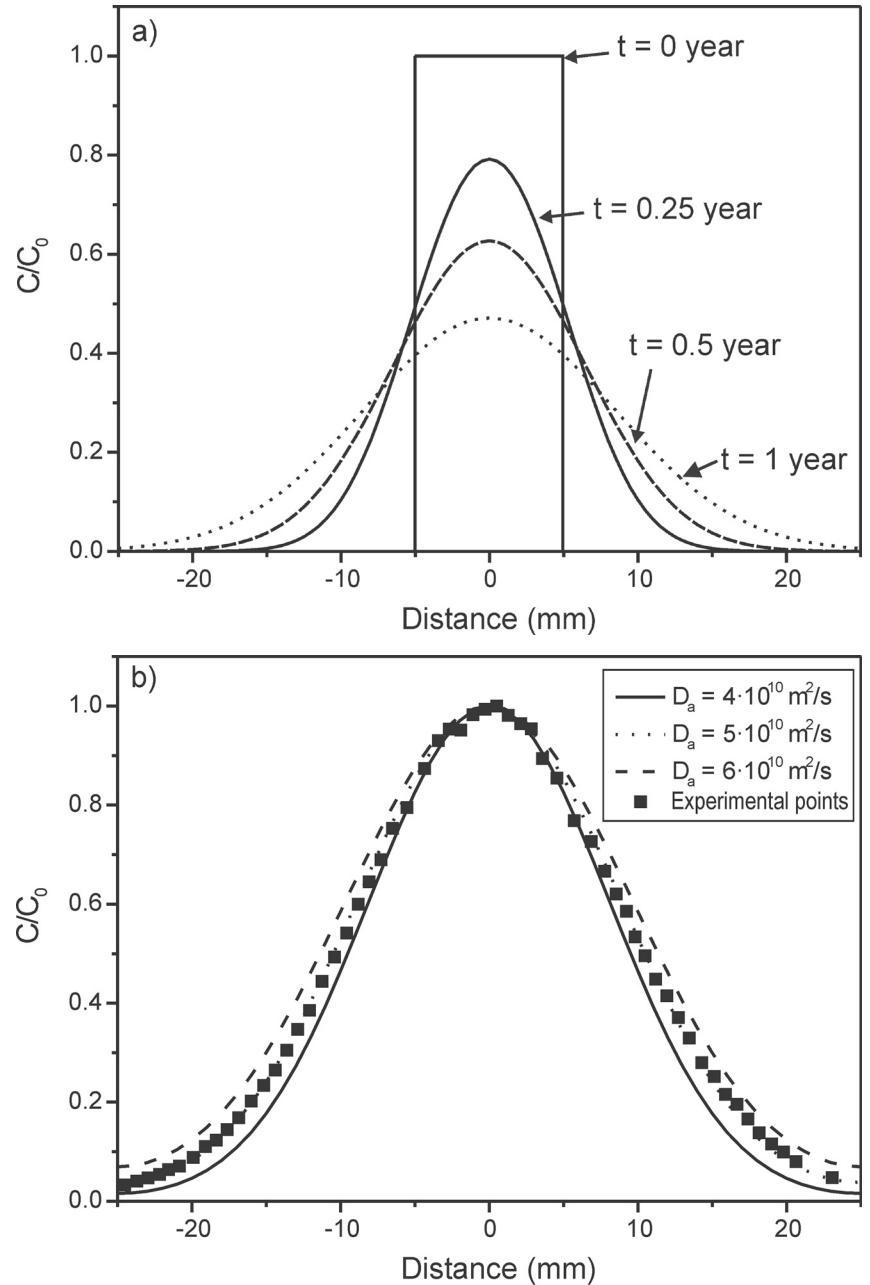
Fig. 7.- Concentration vs. distance curves for a extended source of limited thickness as a function of time. b) Experimental results obtained using HTO at dry density of 1.7 g/cm³.

Fig. 7.- Curvas de concentración vs. distancia para una fuente de un cierto espesor, en función del tiempo. b) Resultados experimentales obtenidos utilizando HTO a una densidad de compactación de 1,7 g/cm³.

constant concentration is measured. After the experiment, the plug is sliced and each slice is weighed to determine its volume. Then, the clay is transferred to a centrifuge tube and a volume of water added. The tubes are kept in continuous stirring during three days and, after this period, the samples are centrifuged and the activity in the supernatant is measured. Accessible porosity in each slice can be calculated using the following equation:

$$A = V \cdot C_R \cdot \phi \qquad (25)$$

where A is the activity in the bentonite slice, V the volume of the slice, C_R the concentration in the reservoir and ϕ the accessible porosity (to distinguish of total porosity, ε).

Each slice provides a value of the accessible porosity, which allows calculating a mean value and its error from a single experiment. Saturation techniques can provide very good results in the case of neutral species like HTO and anionic species (not with high density samples), but they are extremely time consuming for strongly sorbing cationic species or anionic species when using high dry-density samples.

Through-Diffusion experiments at steady-state conditions, using the time-lag method, have been shown to be very useful for the determination of effective diffusion coefficient, but they are less precise in the determination of the accessible porosity. Accessible porosity can be
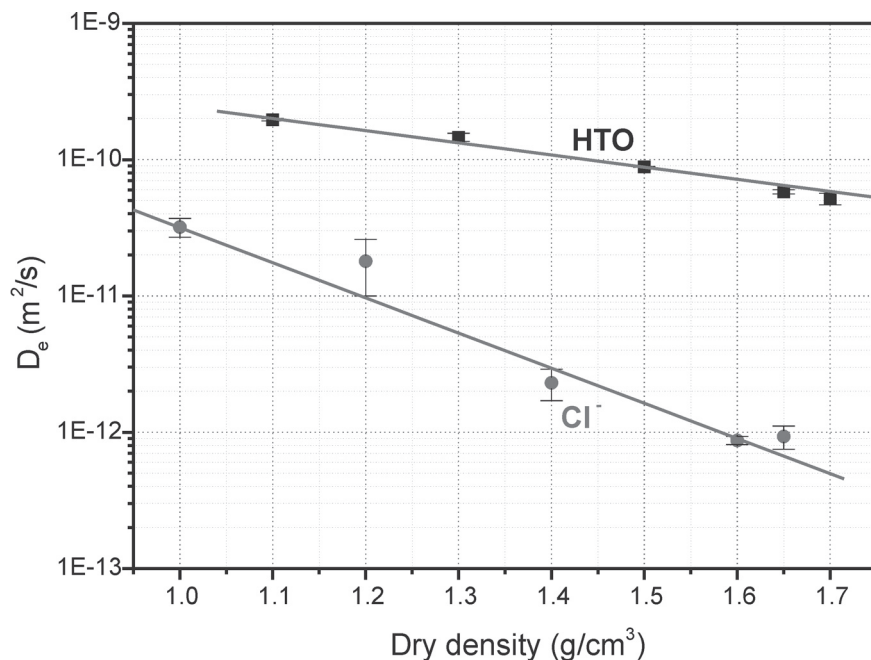
Fig. 8.- Effective diffusion coefficients, and its error, obtained with different methods for HTO and Cl⁻ as a function of clay density. The exponential fits are included as a continuous line.

Fig. 8.- Coeficientes de difusión efectivo, y su barra de error, de HTO y Cl⁻, obtenido mediante diferentes métodos en función de la densidad seca de la arcilla. Las líneas continuas representan el ajuste exponencial obtenido.

obtained using equation (18), for conservative elements, because the rock capacity factor is equal to the accessible porosity. But the error in determining rock capacity factor for samples with low sorption capacities or porosities (α close to zero) may be significant, resulting again in large errors in D_a, (Grathwohl, 1998).

In Through-Diffusion experiment in which the concentrations in the reservoirs change with time, when the tracer concentration in the out-reservoir is significant, it can be ensured that the concentration profile within the clay pore water is linear. In this case, pore water concentration at any point in the sample can be calculated interpolating between concentrations at the extremes (in- and out-reservoirs concentrations). As a consequence, for each slice the average tracer concentration in the pore water can be predicted, and using equation (25) the accessible porosity can be calculated.

5. Summary of experimental results and discussion

5.1. Conservative tracers

As previously mentioned, the main conservative tracer studied was HTO, representative of neutral species. A summary of the results obtained (D_e, D_a and accessible porosity) with HTO is shown in Table 1. Figure 8 and figure 9 shows the comparison of the D_e (Fig. 8) and accessible porosity (Fig. 9) obtained with HTO and ^{36}Cl⁻ at different bentonite dry densities.

The main methods used with HTO were through-diffusion with variable concentration in the reservoirs and in-diffusion with constant concentration in the reservoir. Saturation experiments, to determine the accessible porosity, were performed at several clay dry densities, and the results can be compared with the theoretical total porosity value present in the last column of Table 1. The values represent an average value obtained from several experiments at the same conditions. The experimental results clearly show that for HTO the accessible porosity is always approximately equal to total porosity (Fig. 9).

On the other hand, it is of special interest the study of anions because performance assessment calculations of spent fuel repositories have shown that doses are mainly controlled by non-sorbing anionic species (^{129}I⁻ and ^{36}Cl⁻). The behaviour of anionic species (Cl⁻, I⁻ and SO$_4^=$) was studied in FEBEX bentonite.

Table 2 shows the experimental results obtained with different anionic species. As in Table 1, the results represent the average value obtained in different experiments. For low-density samples through-diffusion experiments with variable concentration in the reservoirs were performed to obtain the effective diffusion coefficient, and saturation experiments were done to obtain the accessible porosity. For density greater than 1.4 g/cm³ through-
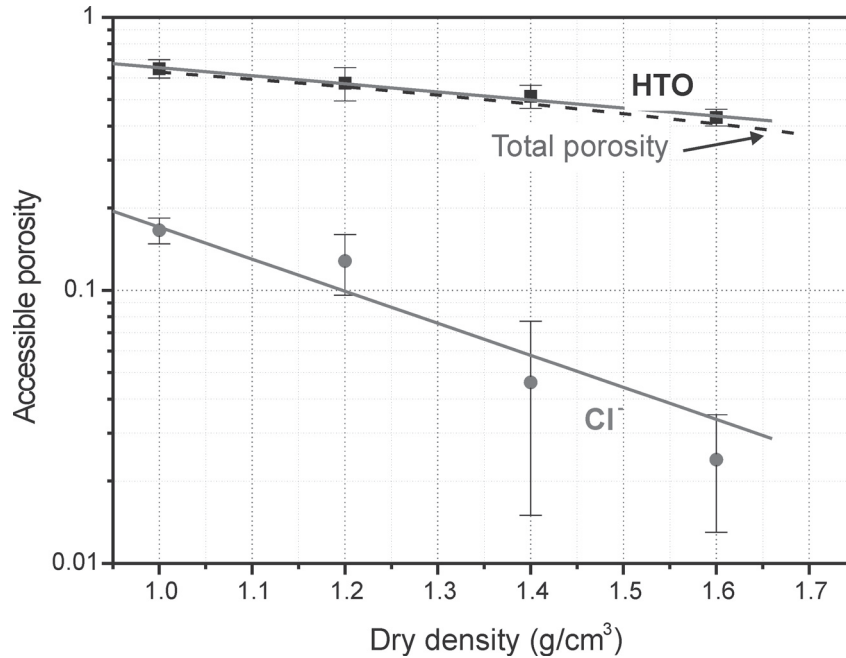
Fig. 9.- Accessible porosity obtained with different methods for HTO and Cl⁻ as a function of clay density. The continuous lines correspond to the exponential fits of the experimental values and the dotted line corresponds to the total porosity of the clay, equation (14).

Fig. 9.- Porosidad accesible de HTO y Cl⁻ obtenida mediante diferentes métodos y en función de la densidad seca de la arcilla. Las líneas continuas representan el ajuste exponencial de los valores experimentales, y la línea de puntos la porosidad total de acuerdo con la ecuación (14).

diffusion experiments with constant concentration in the reservoirs were performed for D_e determination. The accessible porosity was obtained by time-lag methods or considering a linear profile into the clay plugs in TD experiments at the end of the experiment, or both methods. The apparent diffusion coefficient presented in the last column was calculated taking into account the ratio between the effective diffusion coefficient and the accessible porosity, equation (11) for conservative tracers. For all

Dry density (g/cm³)	D_e (m²/s)	D_a (m²/s)	ϕ (%)	ε(%)
1.0			64.9±0.5	63.0
1.1	1.96±0.04E-10	3.3±0.1E-10		59.3
1.2			57.4±0.8	55.7
1.3	1.46±0.10E-10	3.1±0.1E-10		51.9
1.4			51.4±0.5	48.1
1.5	8.86±0.06E-11	2.6±0.1E-10		44.4
1.6			43.0±0.3	40.7
1.65	5.80±0.20E-11	1.6±0.5E-10		38.9
1.7	5.16±0.50E-11	2.6±0.1E-10		37.0

Table 1.- Summary of the experimental results for HTO at different bentonite clay density. The last column shows the theoretical porosity at the given density.

Tabla 1.- Resumen de los resultados experimentales obtenidos con el HTO en función de la densidad seca de la bentonita. La última columna presenta la porosidad total para cada densidad considerada.

the considered elements, accessible porosity in the case of anionic species is significantly smaller than for HTO. Furthermore, figure 9 shows that the Cl⁻ accessible porosity decreases significantly with increasing clay dry density.

As mentioned before, the measured accessible porosity for HTO is roughly equal the total porosity of the FEBEX bentonite at different dry densities. Since total porosity is easy to calculate with equation (14), when one of the diffusion coefficients (effective or apparent) is measured the other coefficient can be calculated using equation (11) and giving to ϕ the value of the total porosity (ε). Therefore, a simple diffusion model in pore water fully explains experimental results for HTO.

Chloride ions have a very different behaviour compared with HTO in FEBEX bentonite (García-Gutiérrez *et al.*, 2004). In fact, even at low densities only a fraction of total porosity is accessible for chloride. If dry density increases, the accessible porosity for chloride decreases rapidly, and at the density of 1.65 g/cm³ its value is between 2% and 3%, while the total porosity is close to 40%. Similar values are obtained for the other anions studied (Table 2). These results show that a significant anionic exclusion occurs.

It is usually accepted that anionic exclusion decreases when the pore water ionic strength increases. The electrostatic effect may be higher at lower clay density be-

Element	Dry density (g/cm³)	D_e (m²/s)	ϕ (%)	D_a (m²/s) (calculated)
³⁶Cl⁻	1.0	3.2±0.5E-11	16.6±1.8	1.9E-10
³⁶Cl⁻	1.2	1.8±0.8E-11	12.8±3.2	1.4E-10
³⁶Cl⁻	1.4	2.3±0.6E-12	4.6±3.1	5.0E-11
³⁶Cl⁻	1.6	8.7±0.6E-13	2.4±1.1	3.6E-11
³⁶Cl⁻	1.65	9.3±1.8E-13	2.5±0.3	3.7E-11
I⁻	1.65	8.6±0.4E-13	2.5±0.3	3.4E-11
³⁵SO₄⁼	1.65	1.1±0.7E-13	2.7±1.9	4.1E-12

Table 2.- Summary of the experimental results for Cl⁻, at different clay density, I⁻ and SO₄⁼ at 1.65 g/cm³.

Tabla 2.- Resumen de los resultados experimentales obtenidos con el Cl⁻, en función de la densidad seca de la bentonita, y para I⁻ y SO₄⁼ a 1,65 g/cm³.

cause the overlapping of the double layers of the pore surfaces does not occur, but at higher clay density the ionic strength effect is expected to be less significant. This point is under study.

As can be seen in the Table 1 and Table 2, and figure 8 and figure 9, the effective diffusion coefficients (and similarly the apparent diffusion coefficient) and the accessible porosity show an exponential decrease when the clay density increases. The decrease is significantly more pronounced in the case of Cl⁻. Therefore for each parameter, the experimental values can be adjusted using exponential functions of the form

$$D_{a,e} = A \cdot e^{-B \cdot \rho_d}$$

where A and B are constants and ρ_d is the bentonite dry density. Continuous lines in figure 8 and figure 9 correspond to the exponential fits of the experimental values and the dotted line in figure 9 corresponds to the total porosity of the clay according equation (14). HTO and Cl⁻ accessible porosity, apparent and effective diffusion coefficients in FEBEX bentonite at any dry density can be therefore easily estimated by interpolation.

Table 3 present the fit values of A and B obtained with HTO and Cl⁻ according the above exponential function.

5.2. Sorbing tracers

Through-Diffusion experiment with variable concentrations in the reservoirs and internal source methods (instantaneous planar source, thick source and half-plugs) were carried out with ⁸⁵Sr, ⁹⁰Sr, ⁷⁵Se, ⁹⁹Tc, and ²³³U. In-Diffusion tests were performed with ¹³⁷Cs, ⁹⁹Tc, Re and ⁷⁵Se. Clay plugs with different thickness and compacted at different densities were used. Technetium and Rhenium are considered conservative tracers when they occur as TcO₄⁻ and ReO₄⁻, respectively, as is normal in oxidizing environments. The diffusion experiments were carried in oxic condition and we expected a conservative

behaviour, but the low diffusion coefficient obtained may be an indication that a reduction processes, for instance of Tc(VII) to Tc (IV) a less mobile form with sorption capacity, occurred during the experimental time. Also a very high anionic exclusion effect together with his large molecular sizes could be responsible of these very low diffusion coefficients. The iron contained in the cell can induce the reduction. In the literature not values for Ca-

Element	Diff. Coef.	A	B
HTO	D_e	(2.00±0.40)·E-9	2.09±0.18
HTO	D_a	(2.25±2.19)·E-9	1.65±0.75
³⁶Cl⁻	D_e	(2.56±2.40)·E-9	4.35±0.89
³⁶Cl⁻	D_a	(2.80±1.36)·E-9	2.65±0.43

Table 3.- A and B values needed to adjust the HTO and Cl⁻ effective and apparent diffusion coefficients to an exponential function as a function of bentonite dry density.

Tabla 3.- Valores de A y B necesarios para ajustar los coeficientes de difusión efectivo y aparente del HTO y Cl⁻ a una función exponencial que es función de la densidad seca de la bentonita.

Mg bentonite, as the FEBEX bentonite, were found. The Tc diffusion values for Na-bentonite are one or two order of magnitude higher (Yu and Neretnieks, 1997).

Instantaneous planar source tests were used to determine the diffusion coefficients of europium which is strongly-sorbing tracer.

Table 4 summarises the apparent/effective diffusion coefficients results obtained with compacted FEBEX bentonite at 1.65 g/cm³, using nine different elements and different techniques. The intervals in the given values account for the variations observed in the different experimental configurations. Good agreement was generally obtained. The attention was focused to this dry density because it is the density considered in the Spanish concept of disposal, for the compacted bentonite.

Effective diffusion coefficient values measured with Cs are in the same order of magnitude of the values measured with HTO. Therefore, there is no evidence of "surface diffusion" for cesium in FEBEX bentonite.

The comparison of results obtained, following different methodologies, is very important, because the problems related to each technique can be highlighted and the theoretical consistency among the determined parameters verified.

Finally, it is worth remarking that an effort was carried out to develop new methodologies to obtain simultaneously the apparent and effective diffusion coefficient in the same sample. This objective has been successfully reached for cesium (Cormenzana *et al.,* 2003). Particularly, in the study performed with cesium, the method allows determining simultaneously effective and apparent diffu-

Element	D_a (m²/s)	D_e (m²/s)
Cesium (I)	$(0.9 - 3.3) \cdot 10^{-13}$	$(0.1 - 3.0) \cdot 10^{-11}$
Uranium (VI)	$(0.1 - 4.0) \cdot 10^{-14}$	$(0.6 - 2.2) \cdot 10^{-12}$
Strontium (II)	$(1.0 - 2.0) \cdot 10^{-11}$	$(1.0 - 4.0) \cdot 10^{-10}$
Selenium (IV)	$(1.0 - 3.0) \cdot 10^{-13}$	$(6.0 - 8.0) \cdot 10^{-12}$
Technetium (VII)		$(2.0 - 4.0) \cdot 10^{-13}$
Rhenium (VII)	$(2.0 - 6.0) \cdot 10^{-14}$	
Europium (III)	$(6.0 - 9.0) \cdot 10^{-14}$	
Sodium (I)		$(3.0 - 6.0) \cdot 10^{-10}$
Calcium (II)		$(4.0 - 7.0) \cdot 10^{-10}$

Table 4.- Summary of the experimental results using different radionuclides. Clay dry density oft 1.65 g/cm³.

Tabla 4.- Resumen de los resultados experimentales obtenidos con diferentes radionucleidos. A 1,65 g/cm³ de densidad seca de la bentonita.

sion coefficients in compacted bentonite without reaching steady-state conditions. Basically, this method consists of an "In-Diffusion" experiment in which the concentration profile in the bentonite sample is used to estimate D_a, and the temporal evolution of the solute concentration in the reservoir is used to estimate D_e. This method has several advantages over the typical "Through-Diffusion" experiments, in particular: a) experiment duration is significantly shorter, b) D_a values are measured with greater precision and c) it is not necessary to maintain a constant solute concentration in the reservoir.

One of the aims of future work is to obtain simultaneously apparent and diffusion coefficients in the same sample for other critical elements.

6. Conclusions

Several methods for the determination of diffusion coefficients and accessible porosity for which there are analytical solutions can be easily used in laboratory with satisfactory results. Taking into account the properties of the tracer, the best method can be selected considering its advantages/disadvantages. The complementary use of different methods to obtain the same parameter is important for the validation of the results and to minimise the uncertainties on parameter determination.

For what concerns the tests performed on the FEBEX clay, diffusion parameters have been obtained for conservative (HTO, chloride, iodide, sulphate, technetium and rhenium) and non-conservative (cesium, uranium, strontium, selenium, europium, sodium and calcium) radionuclides.

In particular, for HTO the values of D_a, D_e and ϕ have been measured independently, and it has been found that

the relation between effective and apparent diffusion coefficients for conservative tracers, i. e.,

$$D_e = D_a \cdot \phi$$

is satisfied.

Effective/apparent diffusion coefficient and accessible porosity show, for HTO and Cl⁻, an exponential decrease when the clay dry density increase. Accessible porosities for HTO (for all clay densities) and Cl⁻ (for clay densities up to 1.2 g/cm³) were directly obtained by means of saturation experiments. Alternative estimations of accessible porosity were done in through-diffusion experiments with constant concentration and concentration profile experiments, which provided redundant, although less precise, methods for its estimation. Similar values of accessible porosities were obtained with the three methods.

The accessible porosity for HTO agrees very well with total porosity, which implies that all the pores in compacted bentonite are available for diffusion of neutral species. Different results were obtained in the case of Cl⁻, for which the accessible porosity is significantly smaller than total porosity, even at the lower densities. Results for chloride, and other anions, clearly show that FEBEX bentonite displays a significant anionic exclusion. The effect of pore water composition on anionic exclusion will be studied in the future. The consistency of the transport parameters measured using different methods confirms that these methods are appropriate and the values obtained are correct.

Through-Diffusion tests have proven to be an excellent method for the determination of diffusion coefficients under simple experimental conditions, fundamentally for slightly sorbing species. In contrast, In-Diffusion tests seem more suitable for sorbing species, and internal source methods for strongly sorbing tracers.

Experimental methods that require that steady-state conditions be reached can be very time consuming with cationic elements, and are impossible to use with strongly sorbing elements.

Acknowledgments

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