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On radionuclide retention mechanisms in fractured geologic media

Mecanismos de retención de radionucleidos en medios geológicos

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Abstract

Radionuclide migration in crystalline rocks has been studied for many years because these geological systems present suitable properties to host a deep geological repository of radioactive waste. The performance assessment of a repository needs a detailed understanding of the processes that can affect the contaminant transport to bring them in mathematical models adequately.

Retention processes occurring in the rock act as the most important safety function of these repositories so they deserve a special attention.

In this work, the main retention mechanisms occurring in crystalline rocks will be described, as well as the most common laboratory methodologies to deduce values for the retention parameters. The degree of application to the performance assessment of these concepts and the new tendencies and experimental methodologies to study retention processes will be highlighted. Some examples will be illustrated by experiments carried out by our group at CIEMAT.

Keywords: Radioactive waste repository, radionuclides, retention, sorption, precipitation, diffusion, transport, crystalline rocks.

Resumen

Durante muchos años se ha estudiado la migración de radionucleidos en rocas cristalinas, porque estos sistemas geológicos presentan propiedades adecuadas para albergar un almacenamiento geológico profundo de residuos radiactivos. La evaluación del comportamiento de estos almacenamientos necesita de un conocimiento detallado de los procesos que pueden afectar al transporte de los contaminantes para introducirlos adecuadamente en modelos matemáticos.

Los procesos de retención que existen en las rocas ejercen una de las funciones más importantes de seguridad de un almacenamiento, y por ello precisan una atención especial.

En este trabajo, se describen los principales mecanismos de retención que existen en rocas cristalinas, así como la metodología común de laboratorio para obtener los principales parámetros que los describen. Se definirá el grado de aplicación de estos conceptos a la evaluación del comportamiento y se hará hincapié en las nuevas tendencias y técnicas experimentales aplicables a estos estudios. Algunos ejemplos se ilustrarán mediante experimentos llevados a cabo por nuestro grupo en el CIEMAT.

Palabras clave: Almacenamiento de residuos radiactivos, radionucleidos, retención, sorción, precipitación, difusión, transporte, rocas cristalinas.

1. Introduction

Deep geological repository (DGR) systems are needed to isolate residual long-lived radionuclides (RNs) produced by human activity. These systems, in which the waste is buried at several hundreds meters depth in a stable rock environment, must ensure that RN release into the geosphere will not occur or that the activity, that will eventually reach the biosphere, would be within the established limits, not presenting any hazard for human safety.

DGRs are based on the multiple barriers concept, in which the barriers work together to provide redundant containment (See, for example, Chapman and McKinley, 1987; Savage, 1995). In the repository, there are *engineered barriers*, which basically consist on the physico-chemical form of the solid waste, the metal canisters and the buffer or backfill materials (clay and/or cement) that fill the gaps between the canisters and the rock. The *natural (or geological) barrier* is the host rock formation itself, which has to fulfil several characteristics: it has to provide mechanical and chemical stability, low permeability to limit the income of water to the waste and to favour RN retention (Astudillo, 2001).

The last point is critical, in fact, if radionuclides were finally released from the engineered barriers, the large volume of the surrounding host rock will minimise the dose rates reaching the biosphere if, together with dilution and dispersion, retention processes (e.g. sorption, precipitation, matrix diffusion) occur.

Since the retention of RNs within the natural barrier delays or prevents RN migration, it can be considered one of the most important safety functions of the deep geological repository.

Several interdisciplinary studies have to be carried out to evaluate the overall capacity of a particular site to confine the waste and minimise the radioactive release. The principal RN transport mechanisms will be different depending on the type of geologic formation and on the existing physico-chemical conditions (Miller *et al.*, 2000). The most favourable hosts rocks are clays or salt formations, volcanic tuffs and crystalline rocks.

In particular, crystalline rocks are (or have been) under study in different European countries (Sweden, France, Finland, Switzerland, Spain, UK) and also in Canada, Japan and USA. Finland approved in the year 2001 the disposal for high-level waste in the location of Olkiluoto after the study of different possible sites (Vieno and Nordman, 1999) and Sweden has to select the possible site for waste disposal before 2008 amongst two granitic locations (Oskarshamm or Forsmark).

The performance and the safety of such systems can be predicted over the timescales required, only if a deep knowledge of all the processes that can affect the RN migration within the engineered and natural barriers exists. Furthermore, it has to be adequately brought in mathematical models.

The needed information is generally obtained by means of laboratory experiments and field data, in addition to the observation of the behaviour of natural geological systems (Smellie and Karlsson, 1999).

The main advantage of laboratory experiments is that they serve to improve our understanding of specific mechanisms under relatively well-defined conditions, since the dependence of RN migration on individual critical parameters can be tested and modelled. The main disadvantage of the laboratory studies lies on the fact that the temporal and spatial scales are relatively small and the question on the representativity and transferability of laboratory data to the real system (up-scaling) arises.

Field studies play an important role because, apart from providing site-specific data, allow investigating the migration processes at a spatial scale larger than the lab one and under almost “real” conditions. Successful research programmes are often based on a continuous feedback from lab to *in situ* data that synergycally provide an improvement of the mechanisms understanding.

The most important in–situ study executed in Spain, and focused on RN migration in granitic formations, was the “El Berrocal” project (Rivas *et al.*, 1997). It was carried out in a granitic pluton located at the southern edge of the Spanish Central System (Toledo). Different types of studies were made there, including tracer tests with conservative and non radioactive tracers such as fluoresceine, DTPA-Gd and deuterium (García-Gutiérrez *et al.*, 1997).

In Europe, two important underground research laboratories (URLs) are located in crystalline environments: Grimsel (Switzerland) and Äspö (Sweden). In these laboratories research programmes have been carried out for approximately two decades (McKinley *et al.*, 1988; Hadermann *et al.*, 1988; SKB, 1996). To highlight the migration mechanisms of critical RNs, several transport experiments, with a large variety of RN and homologues, were carried out in situ at these URLs (e.g. Eikenberg *et al.*, 1998; Winberg *et al.*, 2000; Smith *et al.*, 2001; Möri *et al.*, 2003).

The uncertainties on the temporal scales can be partially solved by the observation of geological natural analogues but the conceptual and predictive mathematical modelling represents a fundamental issue. The more precise and sound are the input data, the more reliable the model predictions will be; the experimental approach used to study the transport processes and the application of new and more sensitive techniques is therefore very important.

The aim of this paper is to summarise the main processes affecting RN migration in a crystalline medium, paying special attention to retention mechanisms. An overview of the present state of the art of their knowledge and their application to PA is presented. In particular, the way in which the most important transport parameters are most commonly obtained is described and discussed. The new tendencies and approaches for the experimental studies related to these issues are highlighted.

2. Radionuclide migration in fractured crystalline rocks

2.1. Main transport parameters

The principal way by which RN may migrate is being dissolved in the groundwater. The chemistry of the water (salinity, pH, Eh, complexing agents) is one of the main parameter controlling the aqueous speciation RNs and their mobility.

In crystalline rocks, fractures play an important role in the transport because the permeability of a fracture network is greater than the permeability of the rock and therefore they can be highly effective pathways for transport. A continuous open fracture would provide a virtually unobstructed travel path for contaminants. In the real case, different mechanisms exist as multiple flow paths, dispersion, sorption or diffusion into immobile water regions that are able to spread and dilute the concentration of the RNs in the fracture and cause their retardation.

In the literature, many very good works exist describing the basic concepts of transport in fractured porous media and the different modelling approaches (Tang *et al.*, 1981; Tsang and Tsang, 1987; Moreno *et al.*, 1990; Bear *et al.*, 1993; Moreno and Neretnieks, 1993; National Research Council, 1996; Gylling, 1997; Selroos *et al.*, 2002), from the classical advection-dispersion model, to alternative stochastic or channel models. The discussion on the difference between these models and their limitations under different conditions is a very broad issue and it is beyond the scope of this work.

For the sake of simplicity, a basic 1D description of the advective RN transport along a single fracture will be given below, just to highlight the most important parameters that have to be taken into account to describe RN migration. The following equation (Skagius, 1992):

$$R_f \frac{\partial C_f}{\partial t} = D_L \frac{\partial^2 C_f}{\partial x^2} - V_f \frac{\partial C_f}{\partial x} - R_f \lambda C_f + \frac{2D_e}{b} \frac{\partial C_p}{\partial z}\bigg|_{z=\frac{b}{2}}$$

(Eq. 1)

where:

C_f= Tracer concentration in the fluid in the fracture [M/L^3]

C_p= Tracer concentration in pore water in the matrix [M/L^3]

D_L= Dispersion coefficient [L^2/T]

V_f= Fluid velocity in the fracture [L/T]

D_e= Effective diffusion coefficient in the porous matrix [L^2/T]

b = Fracture aperture [L]

t = Time [T]

λ = RN decay constant [T^{-1}]

x = Distance along the fracture [L]

z = Distance into rock matrix [L]

R_f= Retardation factor [-].

considers as main transport/retention processes: longitudinal hydrodynamic dispersion in the fracture, sorption onto the fracture surface, unlimited diffusion from the fracture into the porous rock matrix, and sorption within the rock matrix.

The initial conditions for the solution of the transport equation (Eq.1) are.

$$C_f(x,0) = 0 \qquad C_p(x,z,0) = 0$$

where zero concentration of solute in fracture and matrix is fixed at t=0.

The boundary conditions are:

$$C_f(0,t) = f(t) \qquad C_p\left(x,\frac{b}{2},t\right) = C_f(x,t)$$

$$C_f(\infty,t) = 0 \qquad C_p(x,\infty,t) = 0$$

The fracture characteristics are schematically summarised in figure 1.

Sorption on the fracture surface causes a retardation of the RN with respect to the water flow. The retardation factor can be described as:

$$R_f = 1 + \frac{2K_a}{b}$$

(Eq. 2)

where K_a [L] is the so-called "surface sorption distribution coefficient", which represents the partitioning between the amount of RN (C_{RN}) per unit surface and the amount of RN in the liquid phase:

$$K_a = \frac{C_{RN}/A_s}{C_{liq}}$$

(Eq. 3)

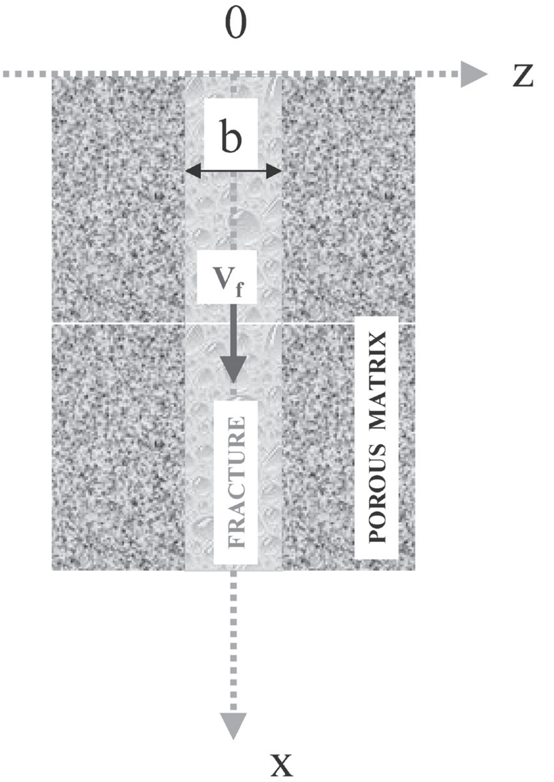

Fig. 1.- Schematic picture of a longitudinal fracture in a crystalline porous medium.

Fig. 1.- Esquema de una fractura longitudinal en un medio poroso cristalino.

The degree of the interaction between the RNs and the rock surface, is controlled by the water flow rate in the fractures and the surface in contact with the flowing water, the "flow wetted surface", FWS (Crawford *et al.*, 2003). In the simple case of a single planar fracture, represented in figure 1, where b is the average spacing of the fracture, the flow wetted surface is defined as the ratio between the fracture surface area and the volume of flowing water, 2/b (Moreno *et al.*, 1997).

If diffusion in the matrix is considered, the equation describing the transport in the porous matrix perpendicular to the fracture is:

$$\frac{\partial C_p}{\partial t} = \frac{D_e}{\varepsilon_p R_f} \frac{\partial^2 C_p}{\partial z^2} \cdot \qquad \text{(Eq. 4)}$$

where R_f is the retardation factor in the matrix due to the sorption, defined by:

$$R_f = 1 + \frac{\rho_b K_d}{\varepsilon_p} \qquad \text{(Eq. 5)}$$

where

K_d = bulk sorption distribution coefficient [L^3/M]
ε_p = matrix porosity [L^3/L^3]
ρ_b = bulk density [M/L^3]

The relation between the effective diffusion coefficient, D_e, and the pore diffusion coefficient, D_p, is:

$$D_e = \varepsilon_p \cdot D_p \qquad \text{(Eq. 6)}$$

and the relation between the pore diffusion coefficient, D_p, and the molecular diffusion coefficient, D, for diffusion in free water is:

$$D_p = \frac{\delta}{\tau^2} D \qquad \text{(Eq. 7)}$$

where δ is the constrictivity of the pores, and τ the tortuosity of the path.

In many experimental works, the apparent diffusion coefficient is (D_a) mentioned. The relation between the apparent and effective diffusion coefficients is: $D_e = D_a \cdot \alpha$, where α, the capacity factor, is defined by $\alpha = \varepsilon_p + K_d \rho_b$.

This simple approximation for diffusion is based on Fick's laws and supposing that the matrix is a homogeneous porous medium.

2.2. Migration experiments

In laboratory, "column" experiments are often carried out to determine these parameters under dynamic conditions. Cylindrical rock pieces, generally presenting a single longitudinal fracture, are used for this purpose. Rock columns are confined and maintained in the desired atmospheric conditions (for example anoxic or with a certain CO_2 content) to maintain or mimic the properties of the groundwater. Figure 2 shows a fractured rock core (10 cm diameter and 22.8 cm length) obtained by drilling from a shear zone in the Grimsel Test Site (GTS, Switzerland), used for laboratory tests by CIEMAT in the frame of the CRR project (Möri *et al.*, 2003). The column was removed from a drillcore from the migration shear zone at the GTS at the end of November 1999. The characteristics of the granite and mylonitic material of the shear zone are largely described in the literature. For details see, for example, Bradbury (1989) and references therein.

The fracture aperture is clearly visible in figure 2 (left) and the column, ready for performing the experiments and located in the anoxic chamber to maintain the groundwater characteristics is shown in figure 2 (right). The groundwater (pH = 9.7; Eh = -200 mV, ionic strength I = $1 \cdot 10^{-3}$ M approximately), is introduced at the top of the column with a HLPC pump and, before of starting the experiment, the stability of the flow rate is checked. Transport experiments are carried out with flow field in the steady-state. The eluted water is periodically collected in previously weighted polyethylene tubes with a fraction collector.

In column experiments, the first step to be carried out is to perform the hydrodynamic characterisation, studying the behaviour of a conservative tracer that does not interact with the rock, as tritiated water (HTO) or fluoresceine. An example of the HTO breakthrough curve obtained in the above-mentioned fractured column is shown in figure 3. The breakthrough curve is expressed as the ratio between the RN concentration at a certain time and the initial RN concentration (C/C_0) as a function of the time or of the eluted volume. Using the conservative tracer, it is possible, in a first approximation, to determine the porosity of the fracture and the velocity of the water directly. The characteristics of the fractured column shown in figure 2 are summarised in Table 1. The simulation of the HTO breakthrough curve was obtained using the Eq.1 and Eq.4. Fitting parameters were D_L and the product $\varepsilon_p D_e$. The modelling is shown as a continuous line in figure 3. The recovery of HTO was approximately a 97 %, in the considered experimental time.

The dynamic behaviour of a certain RN can be studied by comparing its elution curve to that of HTO. Figure 4 shows the comparison of the elution curves of HTO and ^{233}U obtained using the same water flow rate. The retardation factor (R_f), corresponding to the ratio between the velocity of the water (or the conservative tracer, v_{HTO}) and the velocity of the RN (v_{RN}), can be directly obtained by the comparison of both curves. The uranium retardation factor obtained in this experiment, directly comparing the two curves, was:

$$R_f = \frac{v_{HTO}}{v_{Uranium}} = 5.58$$

Fractured column	
Length of the column	22.80 ± 0.1 cm
Diameter	10.00 ± 0.1 cm
Flow rate	5.56 ± 0.15 mL/h
HTO breakthrough peak	10.05 mL / 1.8 h
Fracture width (b)	0.0441 mm
Water velocity (v_f)	12.61 cm/h
Uranium breakthrough peak	51.33 mL / 9.2 h
R_f (^{233}U)	5.38

Table 1: Summary of the characteristics of the fractured column shown in figure 2 and of the parameters obtained in transport experiments with HTO and ^{233}U.

Tabla 1: Resumen de las características de la columna fracturada de la figura 2 y de los parámetros obtenidos en los ensayos de trasporte con HTO y ^{233}U.

The simulation of the uranium breakthrough curve was also obtained using the Eq.1 and Eq.4, as shown in figure 5. The retardation factor obtained by the *best-fit* of experimental data (5.38) is very similar to that determined directly by the curves comparison. The uranium recovery was approximately 37%, significantly lower than that of HTO (97 %), due to retention in the rock.

As mentioned before, column experiments like those above described, were carried out as a part of the laboratory programme designed, as a complement of *in situ* studies, in the frame of the CRR project (Möri *et al.*,

Fig. 2.- Example of a fractured core used for column transport experiments. The core came from the Grimsel Test Site.

Fig. 2.- Ejemplo de testigo fracturado para los ensayos de transporte en columna. El testigo de la figura proviene del Grimsel Test Site.

2003). In this project, the migration behaviour of actinides and fission products in a crystalline fractured media in the presence/absence of colloids was studied at the GTS.

The *in situ* tests were carried out at Nagra's GTS which is located at about 1730 m above the sea level under approximately 450 m overburden thick of crystalline rock. The migration experiments were carried out in a dipole configuration. The dipole length was 2.23 m and the flow field was established between an injection borehole (10 mL/min) and an extraction borehole (150 mL/min).

The radionuclide retardation observed in the field studies increased in the sequence Np(V)~U(VI)<Sr(II)<Cs(I) which is qualitatively consistent with Kd values obtained in laboratory (Geckeis *et al.*, 2004). However, the laboratory and *in situ* behaviour were not totally comparable. In the case of uranium, as an example, the retardation factor observed *in situ* was approximately 1, with a higher recovery (>70 %). The main difference observed in the uranium breakthrough curve with respect to that obtained for the conservative tracer (I^-) was a significant more pronounced tailing.

Apart from the different scale (cm. *vs.* m.) considered, other important difference between the two experiments resides in the water flow rate, much smaller in the laboratory test that tried to reproduce the repository conditions. The water flow rate affects the residence time of the RNs in the fracture (Hoehn *et al.*, 1998) and their interactions with the rock and also the extent of matrix diffusion. Zimmerman *et al.* (2002), for example, observed that sorption increases when the flow rate decreases. In addition, kinetic effects in the RN sorption may be relevant in the retention in the fracture, but they are not often taken into account in transport models. In particular, different authors (Aksoyoglu, 1989; Baik *et al.*, 2003; Missana *et al.*, 2003b) observed kinetic effects in uranium sorption on crystalline rocks. The sorption kinetics is therefore a point that should deserve more attention in future studies as well as the irreversibility of sorption processes (Geckeis *et al.*, 2004). Both effects may affect the tail of breakthrough curves and bias the interpretation of the results.

For what concerns the possible effects of colloids in radionuclide migration in a crystalline fractured medium, some of the main conclusion obtained from the CRR project can be mentioned. It is known that the distance over which the transport may occur depends on the *stability* of colloids and the interactions of colloids with the rock (or *filtration* processes). In Grimsel water chemical conditions (high pH and low salinity), where

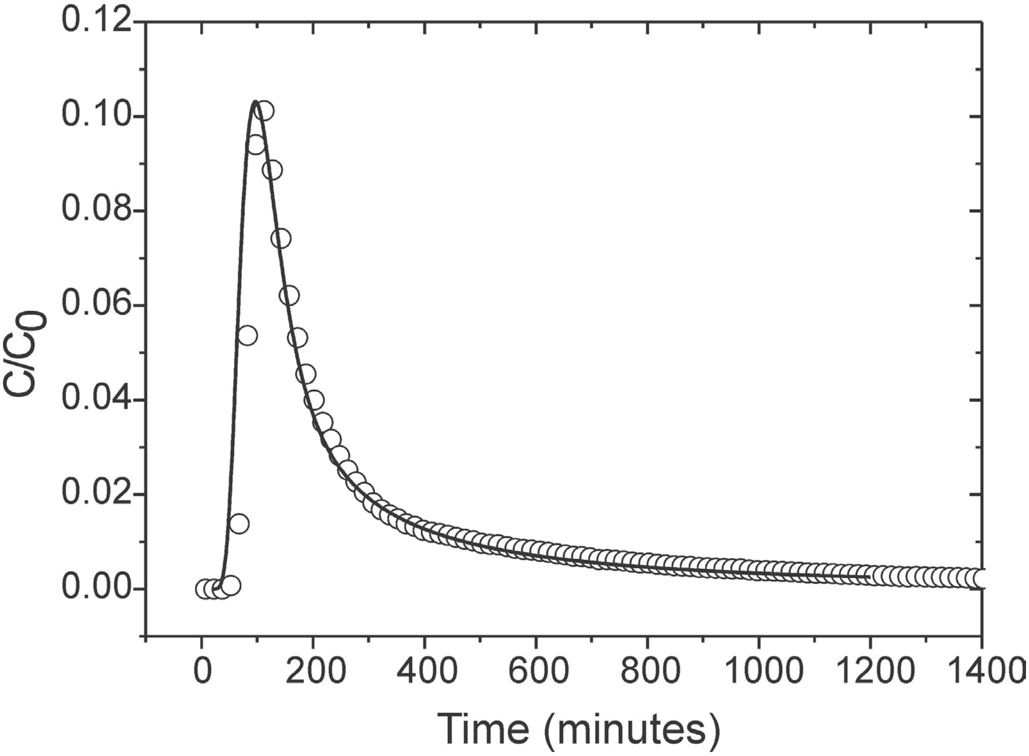

Fig. 3.- HTO breakthrough curve obtained in the column shown in figure 2. (C_0(HTO) = 0.21μCi/mL). The continuous line is the modelling of the curve obtained with an analytical solution of Eq.1 and Eq 4.

Fig. 3.- Curva de elución de HTO obtenida en la columna de la figura 2. (C_0(HTO) = 0.21μCi/mL). La línea continua representa la modelización realizada con una solución de la Eq.1 y Eq 4.

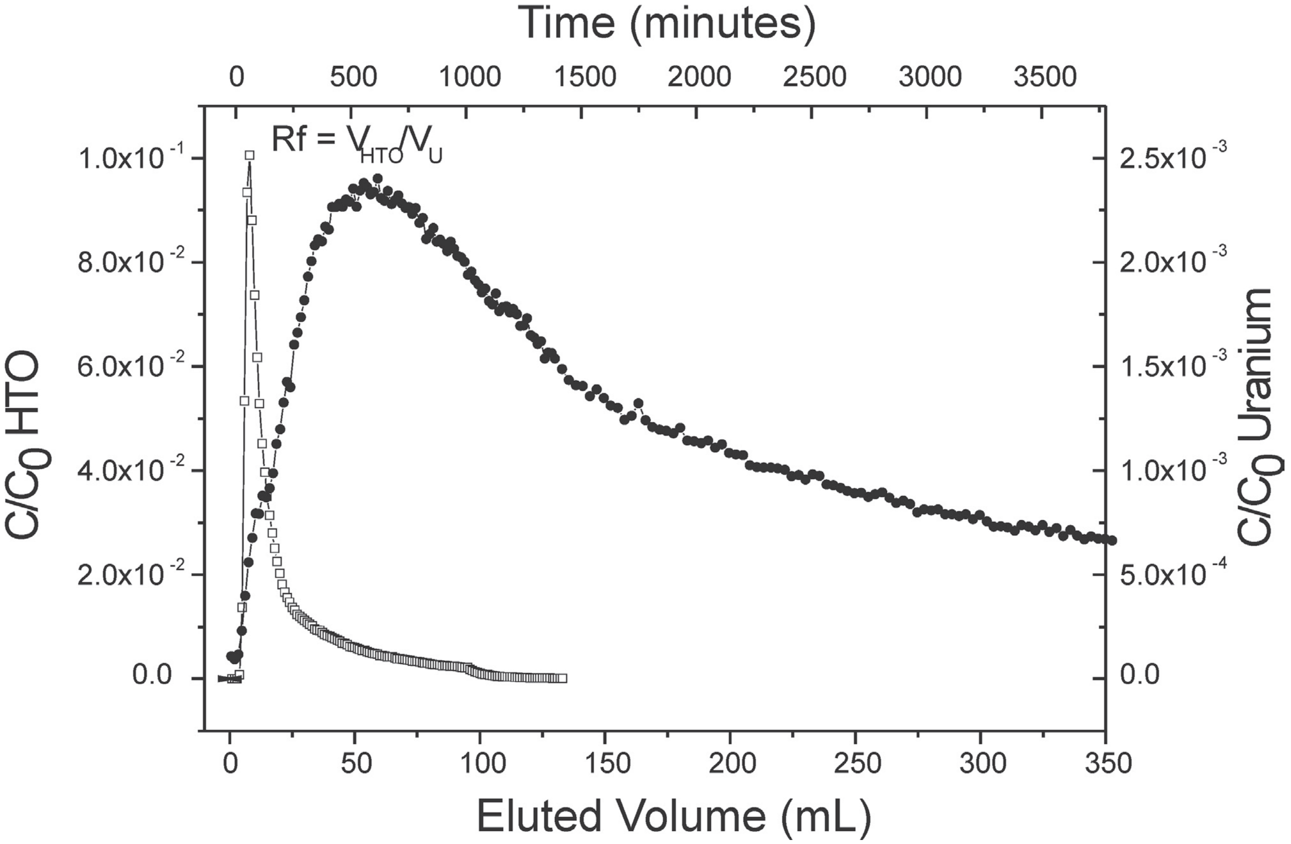

Fig. 4.- Comparison of the (●) U and HTO (☐) breakthrough curves obtained in the column of figure 2. A value of $R_f = 5.58$ was deduced.

Fig. 4.- Comparativa de las curvas de elución del (●) U y el HTO (☐) obtenidas en la columna de la figura 2, para la determinación del factor de retardo ($R_f = 5.58$).

colloid stability is favoured (Missana *et al.*, 2003a), colloid migration did not show retardation, instead the colloid breakthrough was always slightly faster than that of the conservative tracer. However, both field and laboratory experiments, showed that the total recovery of colloids depended on the filtration mechanisms taking place along the colloids flow path and on the residence time in the fracture. The importance to study filtration processes (size exclusion, rock/colloids interactions and diffusion) was highlighted as well as the fact that more detailed studies on these issues could provide experimental data to improve transport models including RNs and colloids.

At present, these models take into account advection-dispersion processes, the sorption of radionuclides onto the rock, matrix diffusion process for the radionuclides and, sometime, the interactions colloid/RN. Anyway, transport models should include the parameter accounting for both colloid/rock and colloid/colloid interactions, include reliable data on colloid diffusion in matrix and it would be desirable that they will account for kinetic processes and the irreversibility of the sorption.

Due to the difficulties to quantify the effect of colloids they are often not included in PA. More details on RN transport associated to colloids are given in a separate work (Alonso *et al.*, this volume).

3. Retention processes: fundamentals and experimental determination of parameters

Since, as mentioned before, the retention of radionuclides within the rock is one of the main safety functions of a DGR, the understanding of retention mechanisms and their description in mathematical models for their quantitative evaluations are fundamental for PA. In the following sections, the main retention mechanisms in crystalline rocks (sorption, surface precipitation, co-precipitation and matrix diffusion) will be defined and discussed.

3.1. Sorption

3.1.1. Definitions

Sorption is the general term used to define an unknown retention mechanism at a solid surface (Sparks, 2003).

By definition, *adsorption* is a process where an accumulation of ions is produced, at the interface between a solid surface and the bathing solution, without the devel-

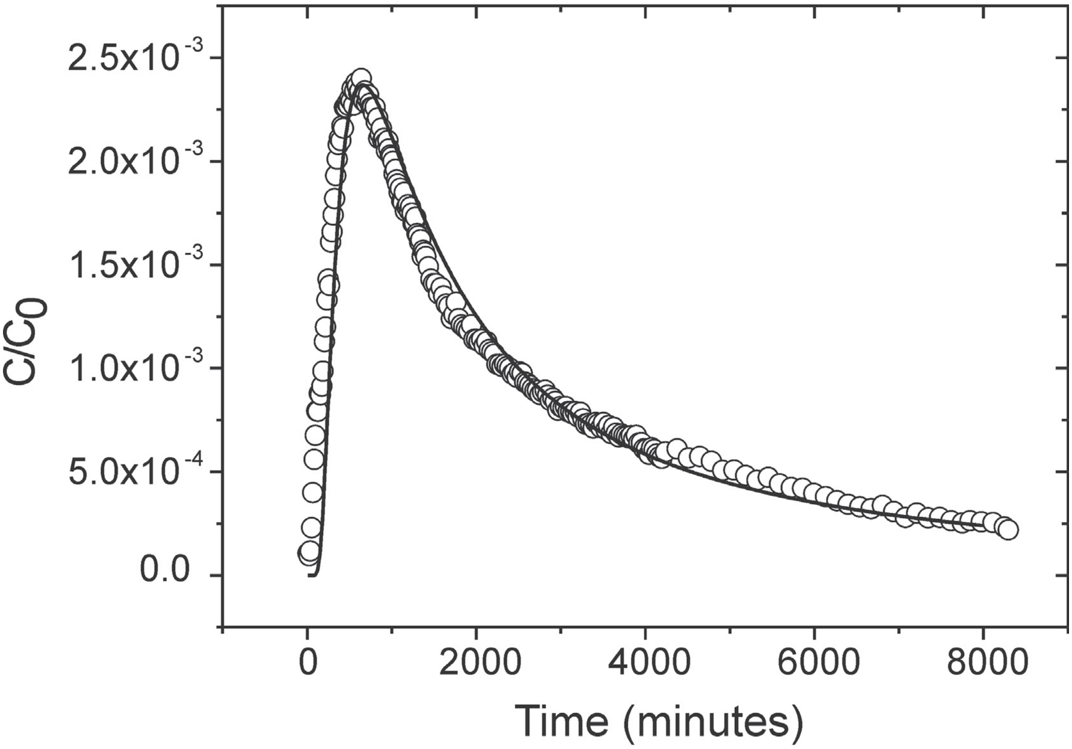

Fig. 5.- ^{233}U breakthrough curve obtained in the infiltration experiment in the core shown in figure 2. (C_0(^{233}U) = 4.4E-5 M). The continuous line is the modelling of the curve obtained with an analytical solution of Eq.1.

Fig. 5.- Curva de elución de ^{233}U obtenida en la columna de la figura 2. (C_0(^{233}U) = 4,4E-5 M). La línea continua representa la modelización realizada con una solución de la Eq.1.

opment a 3D molecular structure (Sposito, 1986). Adsorption does include neither *surface precipitation* nor *polymerization* processes, where 3D structures are usually formed. The term *absorption* defines a process in which ionic species, after the surface interaction, diffuse into the pore space of the solid (Axe and Anderson, 1998). Finally, *ion exchange* is a process in which an ion in the solution is interchanged with another one accumulated at the surface of solids with permanent surface charge, for example clays.

In crystalline rocks, water flows in hydraulically active fractures. The retardation of RN, travelling with water, may take place at the fracture walls, but also on the materials filling the fractures (fracture fillings or fault gauge materials). These materials constitute regions of physico-chemical alterations, generally composed by the weathering materials of the rock itself, but with higher reactive surface area. The fact that fillings are consequence of granite alteration is shown, for example, by the fact that most of the trace elements detected in fracture fillings materials exist also in the granite, as observed, for example in the El Berrocal area (Spain) (Rivas *et al.*, 1997).

3.1.2. K_d-approach

The first step needed to understand sorption processes is to obtain laboratory data, which are generally collected for time scales on the order of day to months.

In laboratory, the evaluation of the sorption capability of a solid for a certain RN is usually obtained by means of static or "batch" experiments. In these experiments, a known mass of crushed/powdered solid (rock or fracture fillings) is mixed with a known volume of solution and a known amount of RN. The partitioning of the RN between the solid and the liquid phase is described by the distribution coefficient (K_d):

$$K_d = \frac{C_{ads}}{C_{liq}} \qquad \text{(Eq. 8)}$$

where C_{ads} is the RN concentration in the solid (mol/g) and C_{liq} is the RN concentration in the liquid phase (mol/mL).

This is a very fast and simple method to obtain values for the sorption parameters.

However, retention parameters are sometimes obtained, in dynamic conditions, using columns made by crushed solids (granite or fault gouge). Through the determination of the retardation factor, R_f, and applying Eq. 5, K_ds can be estimated. Figure 6 shows a small column of crushed rock from the same zone of the GTS in which the fractured column of figure 2 was obtained. The characteristics of these small columns are summarised in Table 2. Considering the geometric volume of the columns and assuming an average density of the fault gouge material of 2.68 g/cm^3 (Meyer *et al.*, 1989), a mean porosity value (ε) of 38.8 % was obtained.

The water used in these experiments was a low ionic strength ($I = 1\cdot10^{-3}$ M) and alkaline (pH = 8.5) synthetic groundwater.

Figure 7 shows examples of breakthrough curves obtained in these crushed rock columns for HTO and Cl- (conservative tracers) and uranium and cesium (non conservative), using similar water flow rates ($Q = 0.35 \pm 0.10$ mL/min). The modelling of these curves was carried out considering an equivalent porous medium approximation. The program used for the analysis of these experimental data is the CXTFIT v2.1 (Toride *et al.*, 1999). More details on these experiments can be found in Missana *et al.* (2003b). The modelling of the curves, showed as continuous line, allowed determining the dispersivity, mean porosity, retardation factors and Peclet number (Pe). The Pe is an indicative of the relative contribution of the mechanical dispersion and diffusion to solute transport. A Pe below 0.4 indicates that the transport is diffusion-controlled, a Pe between 0.4 and 6.0 suggests that diffusion and advection are in transition and both processes are important; and finally a Pe > 6.0 indicates that the transport is advection - controlled. In these experiments the transport was advection – controlled (Pe, determined in HTO tests was 14.6±1.5).

Fig. 6.- Small column for transport experiments with crushed crystalline rock.

Fig. 6.- Columna pequeña para realizar experimentos de transporte en roca cristalina molida.

Column of crushed rock (size < 1.18 mm)	
Length of the column	6.50 ± 0.01 cm
Diameter	8.10 ± 0.1 mm
Mass of crushed material	5.63 ± 0.01 g
Total porosity	38.8 %
Water velocity	1.855 cm/s

Table 2: Summary of the characteristics of the column of crushed rock shown in figure 6.

Tabla 2: Resumen de las características de las columnas de roca molida de la figura 6.

The recovery of both conservative tracers was 100%. It is interesting noticing that the elution peak of ^{36}Cl (Fig.7b) appears slightly before than that of HTO (Fig. 7a) and, in addition, the average porosity obtained from the analysis of the two conservative tracers is different. The average porosity obtained in the experiments with ^{36}Cl (32.7%) is lower than the average porosity obtained for HTO (37.3%). These facts suggest that anionic exclusion exist.

Anionic exclusion is another important mechanism that can strongly affect the migration of radionuclides in the medium. It has been observed by different authors in radionuclide migration tests of different nature (e.g. Siitari-Kauppi *et al.*, 1994; Olin *et al.*, 1997) and 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 $^{36}Cl^-$ (ENRESA, 1997).

Figure 7c presents the normalised breakthrough curve obtained for ^{233}U. Even, also in this case the recovery was near to 100 %, the shape of the curve is not *quasi* gaussian as in the case of HTO and ^{36}Cl. A more pronounced tailing edge is observed which can be due to the sorption of ^{233}U in the crushed rock. A delay in the elution peak with respect to conservative tracers was also observed. By the modelling of the breakthrough curves, a retardation factor of 4.52 was estimated.

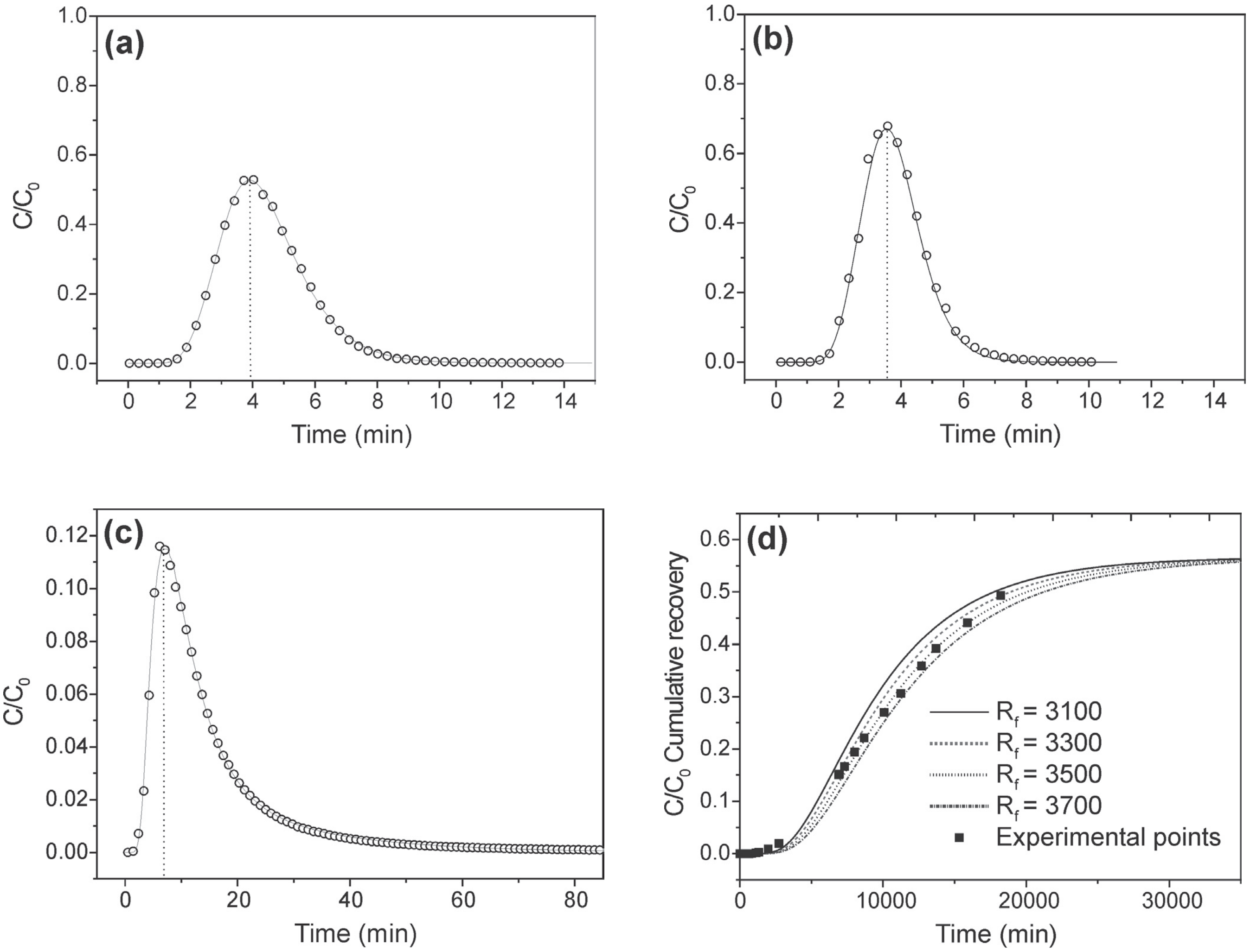

Fig. 7.- Breakthrough curves obtained in the column experiments using crushed rocks with: (a) HTO; (b) ^{36}Cl; (c) ^{233}U. In (d) the cumulative recovery in of ^{137}Cs, obtained in a similar experiment, is presented.

Fig. 7.- Curvas de elución obtenidas en las columnas de roca molida: (a) HTO; (b) ^{36}Cl; (c) ^{233}U. In (d) se presenta la curva acumulada de la recuperación de ^{137}Cs obtenida en un experimento similar.

According with the retardation factor definition:

$$R_f = 1 + \frac{\rho}{\varepsilon} K_d$$

and considering $\rho = 2.68$ g/cm^3 and $\varepsilon = 0.37$ a K_d about 0.5 mL/g is obtained. The K_d value obtained from batch experiments for the same material and the same grain size after a contact time of 1 week was 1.81±0.19 mL/g (Missana *et al.*, 2003b). However, in batch experiments, uranium K_d values tended to increase with contact time and depended on the mean size of the crushed rock.

Figure 7d shows an example of the results obtained with ^{137}Cs. Due to the high sorption onto the rock, the retardation of cesium was very pronounced and the tracer recovery at the end of the experiment was about 55.9 %. A complete breakthrough curve was not obtained but this did not affect the modelling of data, however, the modelling procedure can be better understood, if experimental data are plotted as cumulative recovery. Different theoretical curves were plotted varying the retardation factors and dispersivities (D_L) and the simulations that better reproduced the experimental data were those obtained with a value of D_L = 2 cm^2/min and R_f between 3300-3500, as can be appreciated in figure 7d. Thus, as already done for uranium, a distribution coefficient in the range of 460-487 mL/g was obtained. The K_d value obtained for cesium from batch experiments for the same material and the same grain size after a contact time of 1 week was 449±10 mL/g (Missana *et al.*, 2003b). It is worth mentioning that also cesium K_d values tended to increase with contact time and showed dependence on the grain size.

Even, as reported in the literature, “static” and “dynamic” K_d values are generally comparable within a factor 1 to 4, it is clear that the experimental conditions in which these values are obtained affect the value itself and some uncertainties on the real causes of the observed differences remain.

So far, the K_d-approach has been largely used in PA. Usually PA models use a careful selection of batch K_d values, obtained in site-specific conditions, at lab scale and, generally, in crushed/powdered materials. Since, by means of these batch measurements, it is not possible to distinguish which are the mechanisms involved in RN retention, the K_d represents an empirical value. Precipitation that can be a very important retardation process for some elements (for example uranium, see Read *et al.*, 2004) cannot be handled by the simple K_d-approach. In PA, most of the uncertainties related to the K_d determinations are solved defining "realistic" and "conservative" K_d values.

Actually, K_ds are meaningful only if the adsorption is considered to be linear, instantaneous and reversible. Furthermore, the use of a single K_d value for a certain RN is acceptable only if the geochemical conditions are stable and are not subject to spatial variations along the migration path. In fact, the variability of these conditions in the system greatly influences the sorption properties of RNs.

To predict the sorption behaviour of RNs beyond the particular systems studied in the laboratory, another approach is necessary.

3.1.3. Mechanistic models

In order to overcome the problems related to the K_d-approach, the development of thermodynamic mechanistic models is nowadays under discussion for its application to PA (See for example, OECD-NEA Report, 2001).

Mechanistic models describe the formation complexes between the solid surface and the RN using a thermodynamic formalism. These models represent a significant improvement over strictly empirical descriptions because they are able to account for the geochemical variability of the system, provide better insight on retention processes and may be of great help in supporting a defendable choice of K_d values and above all to estimate their uncertainties in a sound way.

For the basic understanding of the sorption mechanisms the effects of the most important physico-chemical parameters such as pH, ionic strength and radionuclide concentration have to be studied independently, therefore the experimental work is more complicated (and time consuming) than the simple K_d determination.

As reported in Altmann and Bruno (2001), in a mechanistic model it is necessary to define the chemical nature and total amount of different chemical component present in the system (aqueous speciation, redox conditions) and to know the thermodynamic stability constants for each species and the thermodynamic activity coefficients. Sometimes, a wider application of these models has been hampered by a lack of thermodynamic databases.

Before defining the nature of the surface/RN complex and its stoichiometry it is necessary to define the sorption sites, their charge characteristics and density. Different models can be finally used (e.g. Langmuir, 1997). The main difference between the different models lies in the description of the relationship of surface charge (σ) and surface potential (Ψ).

Two main adsorption processes usually considered are ion exchange and surface complexation.

The ionic exchange reactions between a cation B, with charge z_B, which exists in the aqueous phase, and a cation A, with charge z_A, at the rock surface ($\equiv X$) is defined by:

$$z_B A \equiv X + z_A B \Leftrightarrow z_A B \equiv X + z_B A \qquad \text{(Eq.9)}$$

Cation exchange reactions are reversible, fast and stoichiometric. The mass action relation can describe the reaction in term of selectivity coefficients. Following the Gaines and Thomas definition , the selectivity coefficient is expressed by:

$$ {}^{B}_{A}K_{SEL} = \frac{(N_B)^{z_A}}{(N_A)^{z_B}} \frac{(a_A)^{z_B}}{(a_B)^{z_A}} \qquad \text{(Eq.10)}$$

where a_A and a_B are the activities of the cations A and B and N_A y N_B are the equivalent fractional occupancies defined as the equivalents of A or B sorbed per unit mass divided by the cation exchange capacity, CEC, in equivalent per unit mass.

Surface complexation occurs at the surface functional groups of the rock surface. An electrical double layer is formed by the adsorption/desorption of hydroxyl ions (Stumm and Morgan, 1981; Sposito, 1984) which leads to a pH-dependent surface charge. The modelling of an oxide surface is generally carried out with the classical diffuse double layer (DDL) model (Stumm *et al.*, 1970; Huang and Stumm, 1973; Dzombak and Morel, 1990).

The reactions at the surface edge sites mainly involve the amphoteric surface functional groups (SOH). The pH-dependent charge is determined by the following protonation/deprotonation reactions:

$$SOH_2^+ \Leftrightarrow SOH + H^+ \qquad Ka_1 \qquad \text{(Eq.11)}$$

$$SOH \Leftrightarrow SO^- + H^+ \qquad Ka_2 \qquad \text{(Eq.12)}$$

where SOH_2^+, SOH and SO^- represents the positively charged, neutral and negatively charged surface sites, respectively, and Ka_1 and Ka_2 are the intrinsic equilibrium acidity constants. The mass law equations corresponding to the reactions Eq. 11 and Eq.12 are:

$$K_{a1} = \frac{(SOH)\{H^+\}}{(SOH_2^+)} \exp(-\frac{F\Psi}{RT}) \qquad (Eq.13)$$

$$K_{a2} = \frac{(SO^-)\{H^+\}}{(SOH)} \exp(-\frac{F\Psi}{RT}) \qquad (Eq.14)$$

where {} represents the ion activity and ( ) the ion concentrations. Since the activity coefficients for all the surface species are assumed to be equal, the activity of these species can be substituted by their concentration ( ). The exponential represents the coulombic term that account for the electrostatic effects. Ψ represents the surface potential, R the molar gas constant, T the absolute temperature (K) and F the Faraday constant.

In some cases, the electrostatic effects are not taken into account (no-electrostatic models). In this case, the equilibrium constant of the reactions Eq. 11 and Eq. 12 are the one expressed by Eq. 13 and Eq. 14 without the exponential term.

Specific adsorption of cations at these surface functional groups can be described, as an example, with reactions of the following type.

For a monodentate binding:

$$SOH + M^{z+} \Leftrightarrow SOM^{z-1} + H^+ \qquad Kc \qquad (Eq.15)$$

with

$$K_c = \frac{(SOM^{z-1})\{H^+\}}{(SOH)\{M^{z+}\}} \exp(-\frac{F\Psi}{RT}) \qquad (Eq.16)$$

For a bidentate binding:

$$2SOH + M^{z+} \Leftrightarrow (SOH)_2M^{z-2} + 2H^+ \qquad \beta_c \qquad (Eq.17)$$

with

$$\beta_c = \frac{((SOH)_2M^{z-2})\{H^+\}^2}{(SOH)^2\{M^{z+}\}} \exp\left(-\frac{(z-2)F\Psi}{RT}\right) \qquad (Eq.18)$$

Again, in non electrostatic models the exponential term is not included.

The selected model should be tested on a data set obtained under a significantly wide range of experimental conditions (including pH, ionic strength, sorbate and sorbent concentration) and it should be considered valid only if it is able to reproduce the entire data set satisfactorily. The testing of the model on the widest possible range of conditions is probably much more important than the selection of the model itself (Missana *et al.*, 2003c). In fact, completely different model approaches may reproduce equally well the same set of experimental data (Westall and Hohl, 1980).

Kulik (2002) recently proposed an alternative method for the modelling radionuclide sorption on mineral-water interface based on the Gibbs energy minimisation.

So far, mechanistic models have been successful applied to "simple" systems composed by single clean mineral surfaces and pure electrolytes but problems arise with the application of mechanistic models in complex natural solids, as it is a crystalline rock. As compared to purified or single mineral, it is much more complicated to obtain all the parameters needed for their application, in particular to define the identity and quantity of available surface sites.

By one hand, it is possible try to explain the behaviour of the complex system using thermodynamic mechanistic models but considering the overall contribution of the mixture (for example, considering only one type of surface site for a certain rock). This approach may be easy and useful to account for certain variations in the geochemistry of the system but certainly does not provide insight on mechanisms.

A more interesting way to proceed would be to consider that a mixture of several minerals composes the surface. These minerals have to be characterised and, afterwards, their sorption behaviour has to be understood, from a mechanistic point of view, independently. Therefore, it would be necessary try to predict the real K_d of the rock weighting the individual contributions (Duro *et al.*, 2001). This approach is more satisfactory from a scientific understanding point of view but maybe sometime difficult to carry out.

This mechanistic approach has been attempted in some natural systems (e.g., Curtis *et al.*, 2004) but possibly due to the complexity of the system, not so much work can be found in the literature, where thermodynamic sorption models are applied to crystalline rocks. Anyway, if it is recognised that a mechanistic approach would be very useful to support the choice of K_d values for PA (Wingefors and Arthur, 2001).

Since new microscopic spectroscopic and more sensitive analytical methods are being developed and applied to the characterisation of mineral surfaces, more sophisticated models could be utilised and validated in the near future (Koretsky, 2000).

3.1.4. Heterogeneities and up-scaling

Another additional problem related to the retention in crystalline rocks is to find adequate methodologies for the up-scaling of K_d obtained from powdered/crushed minerals to the intact rock and "real" conditions, problem that is somewhat related to the heterogeneity of crystalline rocks.

In crushed solids, sorption strongly depends on the specific surface area of the material, S_A. By definition, S_A that is the ratio between the surface area (A) of a material and its mass (M) and which is also expected to vary from intact to crushed rocks. This seems to be a very important parameter to account for in the up-scaling procedures in RN transport in fractured media, as well as the flow wetted surfaces (Moreno and Neretnieks, 1993).

It is important to remark that in the literature, many sorption data obtained on crushed rocks can be found but much fewer data were obtained using intact rocks (Baik *et al.*, 2003).

The sorption capacity of "intact" rocks is usually expressed as the surface sorption coefficient K_a (Eq. 3).

The relation between bulk and surface distribution coefficients is:

$$K_a = \frac{K_d}{S_A} \qquad \text{(Eq.17)}$$

Baik *et al.* (2003) in their study on sorption of U(VI) in crushed rocks and intact surfaces were not able to compare the two parameters and suggested that possibly different sorption mechanisms are occurring in the two cases. Actually, the real problem can be related to the difficulties in the real estimation of S_A. As a consequence, it is not so straightforward to compare directly the surface sorption coefficient K_a with K_d.

It is interesting noticing that sorption experiments in rock pieces, clearly evidences that each RN presents preferential sorption on certain minerals, and that this heterogeneity in the retention may cause problems for the correct specific surface area determination. All the techniques that allow visualising the region in which the RN are adsorbed may be very useful to treat the problem. One of the classical methods for RN sorption "visualisation" is the autoradiography (Pinnioja *et al.*, 1984; Siittari-Kauppi *et al.*, 1999).

Figure 8 clearly explains the importance of the mineralogical heterogeneity on RN retention in the rock. The upper part of the figure shows a picture of granite coming from the Southwest Spain. In the medium, the regions of the granite surface corresponding to micas (biotites) are evidenced and in the lower part the regions where cesium has been preferentially sorbed, obtained by autoradiography are marked.

It is interesting to notice that most of the activity measured on the surface is not randomly distributed on the surface but it is specially localised on biotites. This "preferential" retention has been observed by different authors, but it was not always straightforward to account for it in a quantitative way. To establish the actual areas interacting with a RN it is necessary to visualise interactions areas as well as to combine sorption studies with mineralogical ones.

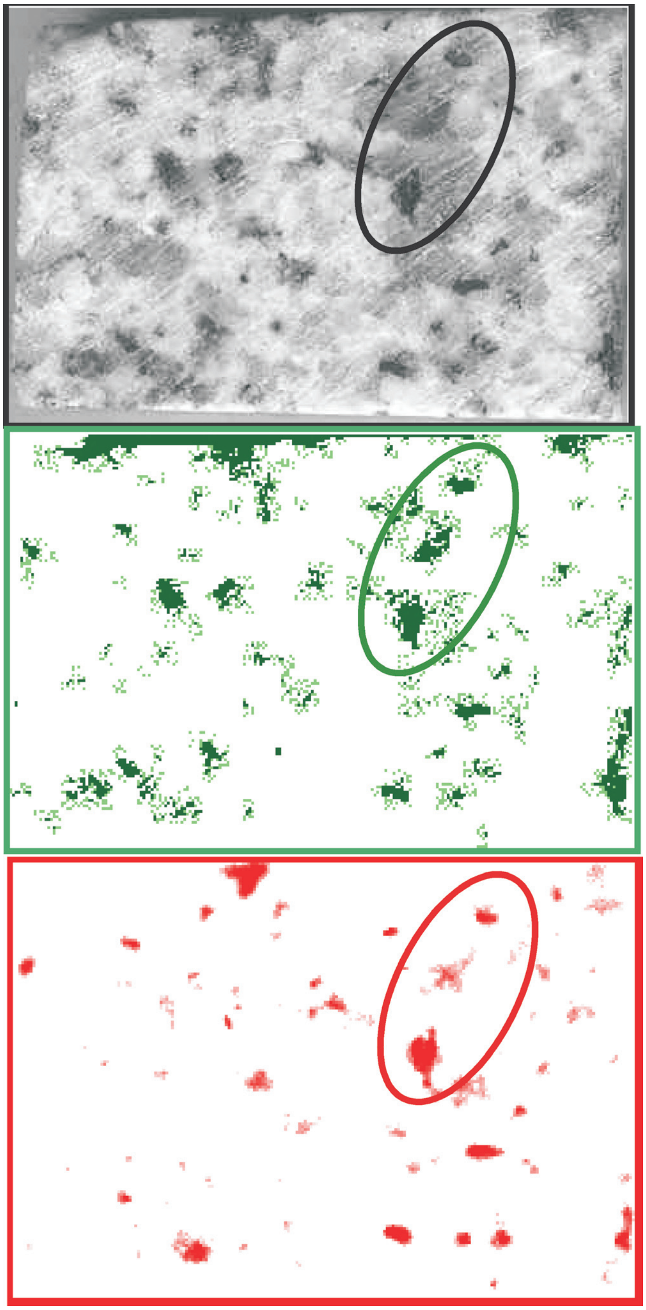

Fig. 8.- Upper picture: image of a granite surface. Central picture: distribution of biotites in the sample. Lower picture: distribution of the ^{137}Cs in the sample obtained by autoradiography.

Fig. 8.- Parte superior: Fotografía de una muestra de granito. Parte central: distribución de las biotitas en la muestra. Parte inferior: distribución de la actividad del ^{137}Cs obtenida mediante autorradiografía.

Additionally, to identify the more reactive minerals will allow focusing mechanistic sorption studies on those particular minerals for a given tracer.

One promising technique that can be used to develop an up-scaling methodology for K_d values is the µPIXE (Particle Induced X-ray Emission). Some details of this technique can be found in Johansson and Campbell (1988).

The technique can be used for identifying and quantifying the reactive surface minerals, since a mapping of single elements on the solid surface, with a resolution of few parts for million, can be obtained. In this way, the surface normalized distribution coefficients (K_a) could be calculated for every single mineral. Finally, this should be also compared with K_a determined in dynamic column experiments and related to the bulk distribution coefficient, K_d.

Figure 9 shows an example of µPIXE analysis of a Grimsel granite surface in which uranium was adsorbed. Also in this case it is clear that the uranium distribution on the surface is not random but it is related to particular minerals, in particular iron or Ti bearing materials (Alonso *et al.*, 2003). The identification of the minerals at the surface can be made simultaneously, observing the distribution of the most important elements (Al, Si, Ca, Mg, Fe…). Different studies are ongoing on this issue at CIEMAT.

Additional efforts are still needed for an appropriate quantification of RN heterogeneous sorption.

3.2. Surface precipitation and co-precipitation

3.2.1. Definitions

As the amount of a ion sorbed on a surfaces increases, sorption can proceed from monolayer adsorption to surface precipitation with the formation of a 3D structure (Sparks, 2003). Precipitation on a solid surface can occur when the solution become saturated and the surface acts a nucleation site but, in some cases, precipitation occurs under conditions in which, in absence of sorbent, the solution would be undersaturated. This mechanism is referred to as surface-induced-precipitation (Towle *et al.*, 1997). In general, at low surface coverage, adsorption is the most important process whereas at higher surface coverage *surface precipitation* can become the dominant one. Several studies, based in XAS techniques showed that different elements (e.g., Co, Ni, Pb) forms surface precipitates on different natural solids (oxides, clays…) also in geochemical conditions in which the metal oxide precipitation would not be expected according to thermodynamic calculations (Scheidegger and Sparks, 1996).

If a precipitate is a chemical species derived from a RN in the aqueous phase and ions coming from the dissolution of the mineral it is referred to as *co-precipitate*. The ionic radius of the sorbing RN and the sorbent ion must be similar for the precipitate to form (Sparks, 2003).

3.2.2. Experimental studies

In comparison to adsorption studies much less experimental work is devoted to precipitation and co-precipitation processes. The inclusion in PA models is “hindered” due to the lack of experimental data. From classical batch sorption experiments, it is sometimes difficult to distinguish co-precipitation or surface precipitation from adsorption, therefore the developing of spectroscopic techniques to analyse directly the solid are of great help. Again, to know the spatial distribution of the elements would be important for distinguishing retention mechanisms of RN (Duff *et al.*, 2001).

In field studies carried out at El Berrocal, retention of uranium in Fe-oxydroxides was observed in fracture fillings material and it was explained by precipitation/co-precipitation (Pérez del Villar *et al.*, 1997). In general, for natural uranium, thorium and light rare earth elements (REE) a preferential association with iron-rich mineral phases is observed in nature, whereas heavy REE, are preferentially associated with calcite (Smellie and Karlsson, 1999), this being usually related to co-precipitation. However, without the use of sensitive techniques is difficult to distinguish adsorption from precipitation.

Indeed, surface precipitation and co-precipitation are important retention mechanisms. They can be mostly irreversible processes. In fact as the precipitate ages the release of the RN can be greatly reduced, leading to “immobilisation” in new mineral phases (Smellie, 2002; Stipp, 2002; Read *et al.*, 2004).

3.3. Matrix diffusion

3.3.1. Definitions

Diffusion is the movement of ionic species in the opposite direction to the concentration gradient. This process is usually described by the First and Second Fick’s laws. 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 porous medium itself, the geochemistry of the system (mainly pore water chemistry) and the temperature.

Matrix diffusion is a process by which RNs, flowing in fractures, are able to penetrate the surrounding rock (Neretnieks, 1980). Diffusion into the rock occurs in a connected system of pores and/or micro-fractures where the water is essentially immobile. Since this connected pore space (i.e. matrix porosity) is larger than the fracture volume in which water is moving, matrix diffusion can be considered a very important retardation mechanism in crystalline rocks. Matrix diffusion, furthermore, increases the rock surface area that can contact with RN, favouring

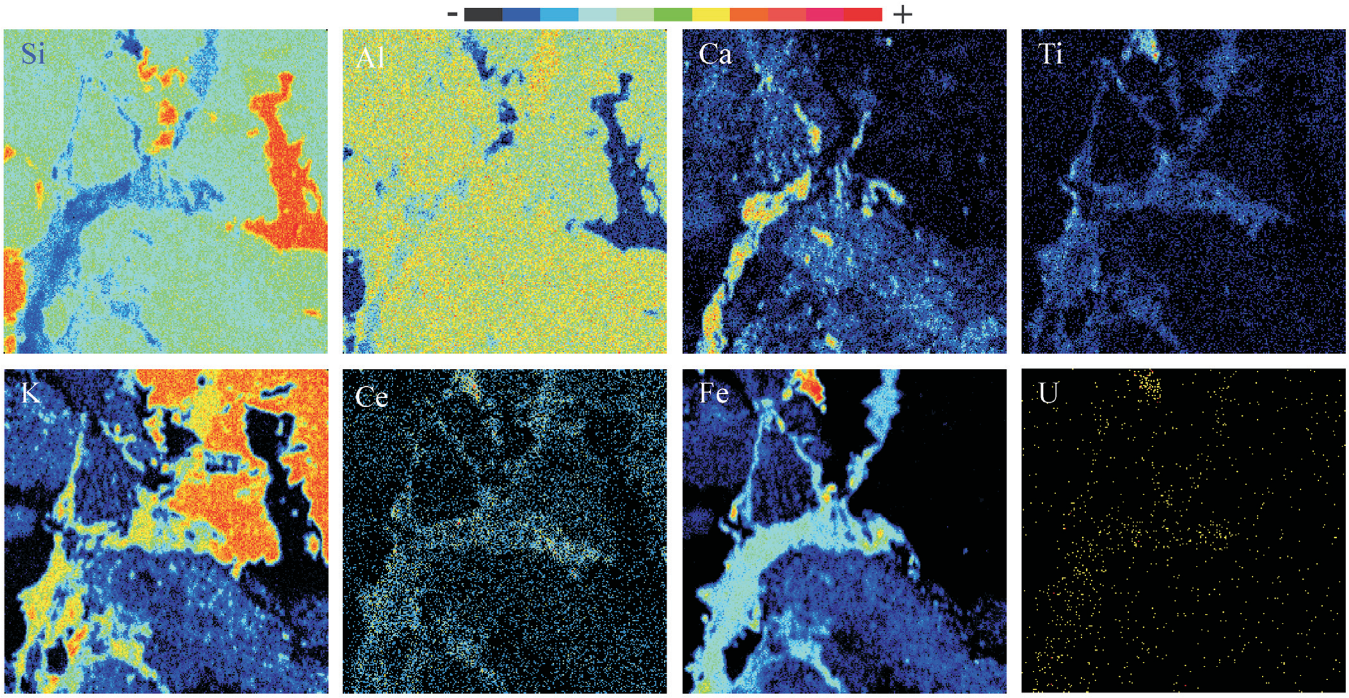

Fig. 9.- Distribution maps of the elements Si, Al, Ca, Ti, K, Ce, Fe and U obtained by µPIXE in a 2x2 mm^2 area of Grimsel granite after 2 days of contact with uranium solution.

Fig. 9.- Mapas de la distribución de los elementos Si, Al, Ca, Ti, K, Ce, Fe y U obtenidos por µPIXE en un área de 2x2 mm^2 de granito de Grimsel, tras dos días de contacto con uranio en disolución.

other retention processes.

The effectiveness of matrix diffusion as retardation mechanism depends on the penetration depth into the rock from the water conducting zones, and it is very dependent on the porosity of the rock, the flow rate and RN diffusivity as well as the flow- wetted surfaces.

Although the theoretical basis of this mechanism seems to be satisfactory established for a long time and it is often included in transport models (Neretnieks, 1980, Lever *et al.*, 1983) more experimental work is needed for concept verification and above all for its quantification in PA.

In most of the models, matrix diffusion is assumed to be Fickian and happen in homogeneous porous medium. Some authors suggested that these assumptions may not be valid (Haggerty, 2002). Simple models in fact do not include the effect of the heterogeneity in rock properties. The uncertainties in the migration pathways for contaminants may make inappropriate the deterministic treatment of transport and therefore stochastic methods have been also developed.

Andersson and Emrén (2003) used the random walk procedure to simulate transport in pieces of rocks. They deduced from their model that matrix diffusion is well approximated by conventional diffusion equation only in rocks with high porosity. They considered conventional approximation no longer applicable in low porosity rocks.

Laboratory diffusion experiments on certain types of heterogeneous rocks were found to exhibit clearly non-Fickian behaviour which was earlier tried to explain by interpretations of the measured out-diffusion curves as combinations of different components representing different diffusivities (Siitari-Kauppi *et al.*, 1997). Recently these curves have been simulated successfully using classical Random Walk and Time Domain Diffusion methods based on measured heterogeneous distributions of porosity (Sardini *et al.*, 2003).

3.3.2. Experimental studies

Different types of laboratory experiments can be carried out to determine the diffusion coefficients of RN but, in dense porous rocks, they are generally extremely time-consuming and sometimes difficult to interpret. Experimental tests on diffusion in crystalline rocks are generally limited to a small number of samples, and relatively few data for diffusion coefficient exist. Ohlsson and Neretnieks (1995) carried out a literature survey of matrix diffusion and sorption data in crystalline materials. Other diffusion data can be found por example in Johansson (2000), Jakob *et al.* (2003) and Winberg *et al.* (2000).

"Classical" laboratory experiments to determine diffusion coefficients of RN and effective porosities are through-diffusion tests (Bradbury and Green, 1985; Skagius and Neretnieks, 1986; Yamaguchi *et al.*, 1997). In these tests, the rate of transport through a section of rock, located between two reservoirs is monitored. Through diffusion tests are preferentially used with non-sorbing or low sorbing RNs. If, in addition, a RN is retained in the rock, appreciable diffusion lengths are obtained only if the experimental time is very large (years).

In-diffusion experiments may be also carried out provided that analytical techniques able to measure the RN profile within the solid are available. Ittner *et al.* (1988, 1990), Johansson *et al.* (1998) and Johansson (2000) proposed a technique in which small pieces of granite were submerged in groundwater traced with the element. After a certain time, the surface of the granite was grinded and RN profile analysed by measuring the powder. Apart from obtaining the RN concentration profiles of the element in the rock, autoradiography of the granite surface were also carried out to evidence the diffusion paths. Also in this case, the needed experimental times were large (from months to years). These experiments additionally indicated that diffusion paths are not uniformly distributed. Some elements preferentially migrated into certain minerals, apart from through defects and grain boundaries. Cesium for example migrated preferentially into biotites and chlorites whereas technetium and iodine migration was not related to any particular mineral (Ittner *et al.*, 1990).

New techniques, particularly attractive, are being implemented to measure diffusion coefficients in crystalline rocks. A promising technique is, for example, laser ablation mass spectrometry (van der Laan and Vliet, 1998).

Due to the short RN diffusion lengths, appropriated analytical techniques could be those normally used for surface analysis. Petit *et al.* (1990) and Toulhoat *et al.* (1996) suggested the use of nuclear ion beam technique for the study of RN diffusion in minerals. These techniques widely used in material science have not been largely applied, so far, to natural rocks, most probably due to the fact that it is not straightforward to account for their heterogeneity. Nevertheless, our group in CIEMAT, in collaboration with the Istituto Nazionale di Fisica Nucleare (Legnaro, Italy) is developing a methodology based in the Rutherford Backscattering Spectrometry (RBS) to measure diffusion coefficients of heavy RNs in granite, in a fast (days) and accurate way. RBS allows studying diffusion processes at the micrometer scale, because it gives in- depth compositional information and is particularly suitable to detect heavy elements inside natural materials. More details on the technique can be found elsewhere (Chu *et al.*, 1984).

Two elements have been studied up to now uranium and europium (Alonso *et al.*, 2003; Alonso *et al.*, 2005) and the satisfactory results seem to indicate that it is adequate for its application with other RNs. These diffusion experiments were carried out on granite sheet of approximately millimitre-sized slices and an average area of 1 cm^2 that were polished to standardise the surface roughness. Laser confocal microscopy was used to observe the micro-fracture network of these samples (Fig. 10).

Granite sheets were immersed in the uranium or europium solutions ($5.71 \cdot 10^{-3}$ M) at three different contact times. Untreated granite areas were also analysed with the RBS technique as reference samples to determine a mean average granite composition for further simulations. The background of uranium or europium, naturally present in the granite, could not be detected with this technique.

RBS measurements were made with a HVEC 2.5 MeV Van de Graaff accelerator using 2.2 MeV a-particles with a scattering angle of 20º.

Figure 11 shows th RBS spectra of granite contacted with the uranium (Fig. 11a) and europium (Fig. 11b) solutions, respectively, after different contact times (5 minutes, 2 hours and 1 day). In both cases, a clear time-dependence in the tracer height and tail is observed, in agreement with a diffusion process. In both figures the RBS spectra of the reference granite is included for comparison. From the RBS direct observation, it can be appreciated that the peaks are rather narrow, thus indicating that there is retention on the granite surface, which can be due to adsorption even if some surface precipitation cannot be ruled out.

The estimation of the penetration depth was obtained from the simulation of the spectra with the XRUMP code (Doolittle, 1986) and the diffusion coefficient of the elements was estimated. From these experiments, the calculated apparent diffusion coefficient was $1.3 \cdot 10^{-13}$ m^2/s for the uranium, and $7.6 \cdot 10^{-14}$ m^2/s for the europium. Considering a porosity of 1% for the granite and K_ds between 0.1 and 10 mL/g, the D_e values will be within the range of $1 \cdot 10^{-12}$ to $1 \cdot 10^{-14}$ m^2/s. These values are comparable with those previously reported for effective diffusion coefficients in crystalline rocks, (from 10^{-13} to 10^{-14} m^2/s) (Yamaguchi *et al.*, 1997; Vieno and Nordman, 1999), obtained with "conventional" methods and with much larger experimental times. Another advantage of the technique is that is possible to carry out the measurement in a single mineral and to compare the behaviour.

Other technique proposed to study the heterogeneous diffusion behaviour of RN in crystalline rocks is X-ray absorption imaging (Altmann *et al.*, 2004).

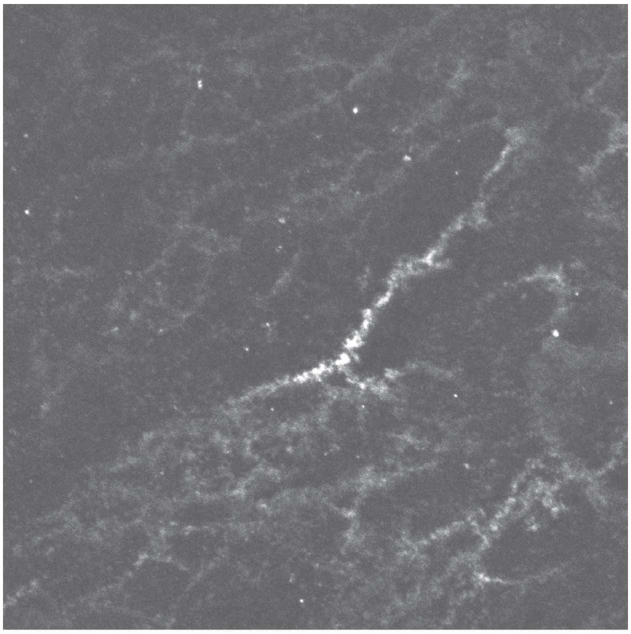

Fig. 10.- Laser confocal microscopy image of the microfracture network in a granite sample used for diffusion experiments. 1024x1024 bits, a bit is 0.3 μm approximately.

Fig. 10.- Imagen de microscopía confocal de la red de micro-fracturas de una muestra de granito utilizada en los experimentos de difusión (1024x1024 bits, un bit corresponde a 0.3 μm aproximadamente).

Matrix diffusion can also be studied in laboratory in column experiments (Hölttä *et al.* 1996). Nevertheless, it is important to remark that, generally in short time scale experiments, where hydrodynamic dispersion dominates the transport, the tracer residence times are short and it is difficult to evidence matrix diffusion, and the parameters of matrix diffusion are often determined by the tail of breakthrough curves from the best fit of the curve.

Other alternative techniques have been developed to study matrix diffusion, for example based on the measurements of electrical conductivity (Ohlsson *et al.*, 2001; Löfgren, 2004), or gas flow (Hartikainen *et al.*, 1995). One of main advantage of these techniques is that large samples can be used, and that it is also possible to carry out these measurements *in situ*.

One of the major problems discussed in the literature concerns the fact that most of the experimental laboratory set-ups consider short diffusion lengths and small samples. It is possible that, in laboratory samples, higher interconnected porosity than that of the pristine rock exist. It is difficult to quantify the degree of sample disturbance affecting the geometrical geophysical and hydraulic properties of the rock matrix, in samples disturbed by collection and preparation (cutting, grinding etc.). Furthermore the un-stressed conditions of the laboratory rock samples cause changes on the matrix porosity.

Several authors determined higher (a factor from 1 to 3) porosities in laboratory than *in situ* (Ota *et al.*, 2003). Higher porosity may lead to higher measured diffusivities an apparently larger degree of retention due to matrix diffusion (factor from 2 to 5 ; Skagius, 1986). These facts can be related also to sample size effects.

Also the determination of the depth of connected porosity in the real conditions is an important issue. The penetration depth is important to calculate the real extent of matrix diffusion and its importance for PA (Park *et al.*, 2001).

Several evidences exists that diffusion accessible porosity exists and for interconnected network that extents to considerable depths in the rock. The penetration of RN may range from few mm to several cm. Greater penetrations usually corresponds with greater alteration degrees of the rock and increased porosity (Heath, 1995). At the El Berrocal site uranium was observed to migrate up to few cm from the fracture into the rock matrix (Menager *et al.*, 1994). At Palmottu (Finland) natural analogue the matrix diffusion model was checked against the mobilisation of long-lived natural elements (Rasilanen and Suksi, 1993; Rasilanen 1997).

Recent work including dating of pure secondary uranium phases at Palmottu and another nearby site clearly indicate postglacial mobilization of uranium from primary (mainly uraninite) and secondary uranium phases (uranophane) in open fractures and the rock matrix and redeposition as uranophane after very short travel distances downwards (scale of meters) (Read *et al.*, 2004)

Several experiments were also carried out *in situ* to study matrix diffusion and improved the general understanding of the process.

3.3.3. Study of the pore space

From the previous sections it has to be recognised that the knowledge of the fluid flow paths, at different scales, is the basis to understand the radionuclide migration and retention processes. At small scales it is necessary to study the geometry of the pore structure (pathway for diffusion, pore connectivity) and the geometry of the microfractures system. At larger scales it is necessary to know the geometry of rock fractures as well as the structural or hydraulic heterogeneities. It is needed to acquire a statistically significant database of physical rock properties to improve our understanding of diffusion processes, and porosities.

Degueldre *et al.* (1996) summarise several methods currently for determining rock porosity. Some of them are non destructive, applicable *in situ* and may provide additional 3D information on the pore structure.

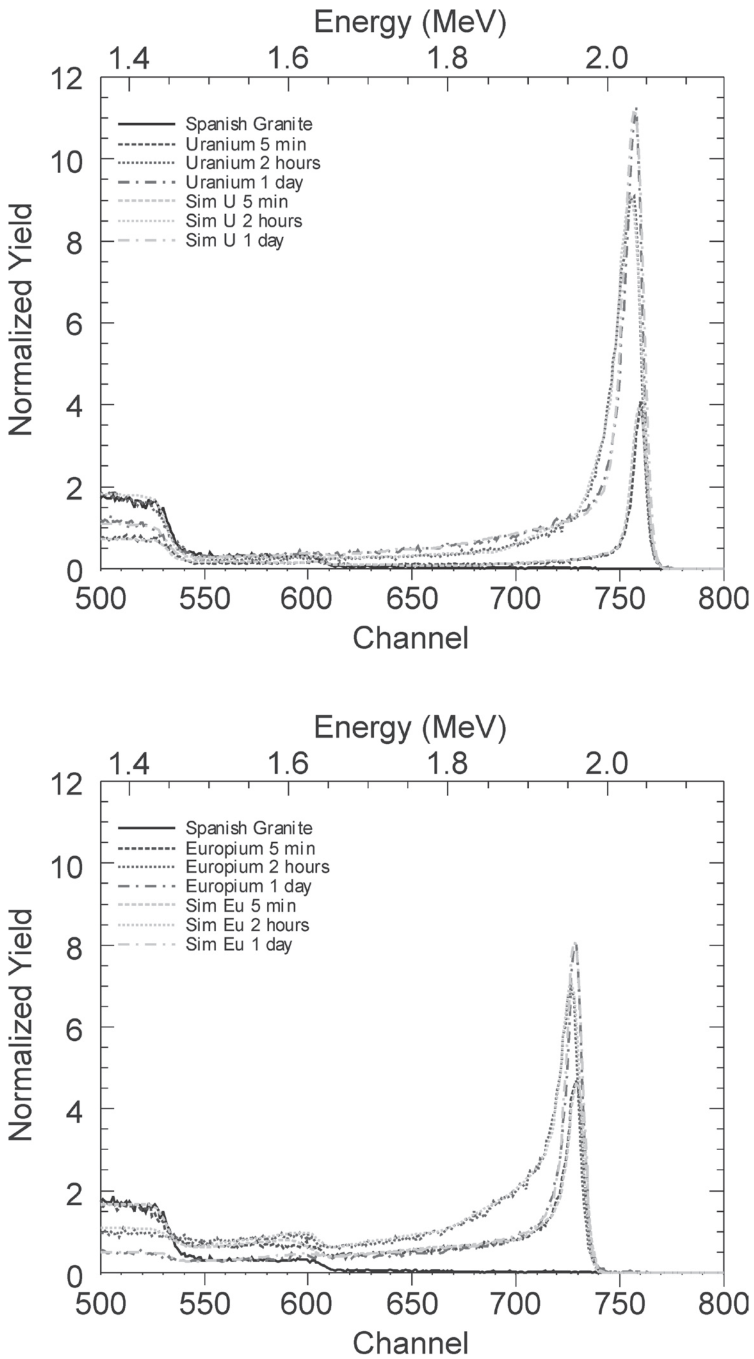

Fig. 11.- RBS spectra obtained on granite after the contact with uranium (above) or europium (below), for different experimental times (5 min, 2 h, 1 day). The spectrum of the reference granite is also included for comparison.

Fig. 11.- Espectros de RBS obtenidos en el granito después del contacto con uranio (arriba) o europio (abajo) a distintos tiempos (5 min, 2 h, 1 día). El espectro de referencia del granito también se incluye.

Quantitative petrography of the samples and impregnation with (^{3}H, ^{14}C) labelled methylmethacrylate and the autoradiographic visualisation of porosity distributions of the samples can be considered a "classical" method. It is usually combined with complementary techniques as optical microscopy, SEM/EDX, FESEM/EDX, confocal laser microscopy, microtomography (Siitari-Kauppi *et al.*, 1998).

Positron emission tomography (PET) and neutron radiography are amongst the newest techniques available to study crystalline materials (Degueldre *et al.*, 1996). Other no destructive techniques are, for example, transmission computer tomography (CT), X-ray microtomography (μXCT). Using the tomography data, the visualisation of cavities and microfracture and network connectivity can be obtained in 3-D. The determination of specific surface areas of certain minerals can be done combining CT tomography with mercury porosimetry (Klobes *et al.*, 1997a; Klobes *et al.*, 1997b).

In situ characterisation by using geophysical logging and tomography helps to get a proper characterisation of the micro fracture network and to construct 3D physical property models of the rock matrix and its visualisation.

Even many efforts have been done, much more work is still required in this area, since it would be of great interest to obtain diffusion coefficients and to correlate diffusion profiles with the physical properties of the rock matrix (Siitari-Kauppi *et al.*, 1994). First attempts modelling the diffusion in a rock matrix consisting of heterogeneous porosity pattern are convincing (Sardini *et al.*, 2003).

4. Final remarks

A significant amount of work has been done during the last two decades to study the RN migration in crystalline rocks and a basic understanding of the key processes that influence RN retention in these media (sorption and matrix diffusion) has been certainly reached.

The experimental work has been carried out both at laboratory and *in situ* scale. Laboratory experiments allowed analysing fundamental processes in controlled conditions and determining the crucial parameters for radionuclide transport. *In situ* studies allowed verifying the degree of knowledge acquired, validating the conceptual models and evidencing potential lacks in theoretical understanding. Furthermore the analysis of data from real systems, both URLs and natural analogues, provided the possibility to identify and quantify processes for time scales not accessible from laboratory experiments.

Some aspects, however, need deeper investigations. In particular uncertainties regarding long-term predictability and system heterogeneities exist.

For PA, transport models should cover hydrodynamic and geochemical processes. The development of a tool to incorporate multicomponent reactive transport to PA would be of great interest. The coupling of hydrodynamic processes (advection, diffusion and dispersion) with geochemical ones is highly recommended (van der Lee and de Windt, 2001; Koretzky, 2000). In fact, kinetically controlled reactions that lead to changes in the aqueous chemistry over time and space are functions of water/rock interactions and may affect also the physical properties of the medium. As an example, porosity and permeability can suffer changes when precipitation or dissolution of minerals takes place or when new-formed colloid clog pores.

As it has been discussed in the previous sections, it would be necessary that geochemical processes considered include aqueous speciation and redox, interface reactions (sorption and ionic exchange) and precipitation/dissolution of minerals and colloids.

The linking between sophisticated hydrologic and geochemical models would offer a great chance to improve the predictability. Moreover, the application of reactive transport models based on mechanistically obtained data would be a great advance in PA.

As summarised in van der Lee and de Windt (2001), nowadays several reactive transport models which are able to manage many geochemical processes are available. The main difficulties related to the use of these models mostly lies in the shortage of reliable input data (thermodynamic data, kinetic or equilibrium constants), which can be obtained only by sound experimental tests. Sometimes the poor conceptual understanding of processes prevents the correct implementation in models (this might be the case of immobilisation processes).

For what concerns the spatial heterogeneity, progresses are needed to take it into account in PA models.

As shown in the previous sections, the heterogeneity of the crystalline rocks, affects the radionuclide retention (both matrix diffusion and sorption) and it is very important to understand how accounting for the heterogeneity to facilitate the integration of some concepts to PA.

New techniques applied to study rock porosities may be of great help for understanding of RN migration paths.

For what concerns adsorption, it would be of interest to develop experimental methodologies to up-scale sorption parameters. Furthermore the application of mechanistic models for the selection of K_d values for PA should be favoured.

For a mechanistic description of sorption, it is necessary to identify which are the minerals that most affect the retention along the flow path, to be able to determine the actual surface area in which retention occurs and the density of available surface sorption sites. Therefore, a combination of sorption, mineralogic and petrographic studies as well as the use of new sensitive techniques is highly recommended.

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