Determination of bentonite colloid diffusion coefficients in a crystalline rock

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I. INTRODUCTION

In a deep geological repository of high-level radioactive waste (HLWR), compacted bentonite is used as engineered barrier between the canisters containing the radioactive waste and the host rock. The compacted clay has low permeability, to limit the water income to the waste, and high sorption capability for many radionuclides, so it is particularly suitable to retard their migration to the biosphere. However, for the long-term performance assessment of a HLWR, the possibility that the formation of bentonite colloids could affect radionuclide transport has to be evaluated as well.

In previous works we proposed a novel approach, based on the application of the Rutherford backscattering spectrometry (RBS), simulating the conditions expected at the bentonite /granite interface of a HLWR, studying the diffusion of some radionuclides in granite, both in presence and in absence of bentonite [1, 2]. It was demonstrated that the presence of clay, generally slowed down the diffusion of the radionuclides, and these results suggested that the clay diffusion occurred had to be related to a colloid transport. So, it is necessary to evaluate and quantify the transfer of colloids to the host rock. To do so, a similar methodology to specifically analyse the colloid diffusion will be applied. In this case, as the bentonite and the granite have very similar composition from the point of view of the RBS, it is necessary to trace bentonite colloids with a heavy element. The colloid movement will be evaluated by trailing the tracer, so it must fulfil several requirements: (a) it has to be a heavy element because of the RBS sensitivity, (b) it has to present almost 100% sorption onto the clay colloids, (c) it is necessary to guarantee that, within the time scales of RBS measurements (days), no tracer desorption from the bentonite colloids to the rock surface could take place. In order to select the tracer, that fulfilled the above-mentioned conditions, complementary batch sorption experiments were performed previous to diffusion studies.

II. EXPERIMENTAL SET-UP

For these previous batch sorption experiments, bentonite colloids were prepared in the laboratory following the habitual method [3], conditioning with NaClO\textsubscript{4} to a final ionic strength of 10\textsuperscript{-3} M, pH 7.52 and a concentration of 0.5 g/l. As first condition, the colloid tracer had to be a heavy element, so Eu, Cs and U, were initially tested. Eu was finally selected because the kinetic sorption studies (spiking the colloids with active \textsuperscript{152}Eu to a concentration of 4,25\texttimes 10\textsuperscript{-6} M and a final pH of 5) revealed that after only 5 minutes, up to 99 $\pm$ 5 % of the Eu was adsorbed onto the bentonite colloids and that the distribution coefficients remained constant at least during one month.

Moreover, the possible desorption from the bentonite colloids to the granite was analysed by placing small pieces of rock in a solution containing the Eu-traced bentonite colloids, and periodically analysing the Eu activity at the rock surface. No desorption from the bentonite colloids was observed within the time scales of interest for RBS studies and even after one week not significantly Eu activity was detected on the granite. Finally, for the diffusion studies, bentonite colloid suspensions (1.9 g/l, NaClO\textsubscript{4} 10\textsuperscript{-3} M, pH 7.52), traced with Eu to a final concentration of 5.71\texttimes 10\textsuperscript{-6} M and a final pH of 4.92, were prepared in the laboratory and kept during 1 week. After that, granite slices were put in contact with the Eu-traced bentonite colloids at different times (5 minutes, 2 hours and 1 day). After proper cleaning, the granite surfaces were analysed by RBS. For comparison, the same diffusion studies were performed with Eu in solution (without bentonite colloids). RBS measurements were made with a HVEC 2.5 MeV Van de Graaff accelerator, at the LNL-INFN, using 2.2 MeV $\alpha$-particles with a scattering angle of 20\textdegree. The spectra simulations were performed with the X-RUMP code.

III. RESULTS AND DISCUSSION

Firstly, the Eu diffusion as solute was analysed. Fig. 1 shows the spectra of the granite contacted with the Eu solution, after 5 minutes, 2 hours and 1 day. A clear time-dependence in the Eu peak height and tail is observed, in agreement with a diffusion process. It can be also appreciated that the peaks are rather narrow, thus indicating retention on the granite surface due to adsorption, but some precipitation cannot be ruled out. The tracer content (in atomic %), as a function of the penetration depth at different contact times in the granite sheet can be estimated from the simulation of the RBS spectra. The calculated diffusion coefficient, representing the travelled distances as function of time, was of 7.6\texttimes 10\textsuperscript{-14} m\textsuperscript{2}/s, value in agreement with values previously reported for solute diffusion in granite [4, 5].

In a second step, granite samples were studied after 5 minutes, 2 hours and 1 day of contact with the Eu-traced bentonite colloids. In Fig. 2 the obtained RBS spectra are
shown, where Eu peaks are detected presenting a clear time-dependence in the tracer height and tail, which is in agreement with a diffusion process.

![Normalized Yield vs Energy (MeV) for Granite and Granite + Eu samples.](image)

**FIG. 1:** RBS spectra of granite after contact with Eu in solution. The performed simulations and the spectrum of the reference granite are also included.

![Normalized Yield vs Energy (MeV) for Granite and Granite + Eu-Bentonite colloids samples.](image)

**FIG. 2:** RBS spectra of granite after contact with Eu-traced bentonite colloids. The performed simulations and the spectrum of the reference granite are also included.

The penetration depth of Eu, as function of the contact time, allowed evaluating the diffusion coefficient, \( D \approx (7.5 \pm 0.1) \times 10^{-17} \text{ m}^2/\text{s} \). Since batch experiments revealed that up to the 98% of the Eu is adsorbed onto the colloids, and no desorption was detected in the experimental times, this Eu profiles measured indicate that the bentonite colloids are able to diffuse within the rock. It is interesting noticing that this colloid diffusion coefficient is several orders of magnitude lower than that measured for Eu as solute, in similar experimental conditions.

The methodology proposed allowed observing for the first time the bentonite colloid diffusion within a low permeability medium. Moreover, the estimated bentonite colloids coefficient gave a value significantly lower than those sometimes applied in theoretical models [6, 7].

**IV. CONCLUSIONS**

In the two studied cases (tracer in solution and sorbed onto bentonite colloids) the Eu diffusion was detected. The diffusion coefficients calculated with this methodology for Eu in solution are equivalent to those measured with conventional diffusion experiments while in presence of bentonite colloids, diffusion is clearly slower. Since the batch experiments indicated that up to 98% of the Eu is adsorbed onto the colloids, and no desorption was detected in the experimental times, the calculated Eu coefficient in presence of colloids, \( D \approx 7.5 \times 10^{-17} \text{ m}^2/\text{s} \) can be taken as the diffusion coefficient of bentonite colloids in the rock.

The methodology proposed allowed experimentally obtaining, for the first time, the colloid diffusion within a low permeability medium. The fact that the calculated diffusion coefficient for colloids is lower than those sometimes considered in theoretical codes, states that other colloid transfer or retention mechanisms need to be experimentally evaluated as well.

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