INTRODUCTION

Nanoparticles (NPs) (< 100 nm) and colloids (< 1 µm) can contribute to contaminant transport in geological media [1]. In fractured rocks, transport mainly takes place by advection in the water flow, being affected by different mechanisms that contribute to particle retention, even at conditions where high retention was not expected, i.e., under unfavorable electrostatic conditions [2, 3].

Colloid diffusion is often accounted for to interpret the tailing behavior of colloid breakthrough curves in transport experiments [4]. Colloid diffusion in rock matrix was demonstrated to be size-dependent [5]. Nevertheless, heterogeneous charge distribution exhibited by different minerals is expected to play a relevant role.

The aim of this study is to quantify the diffusion of nanoparticles on a heterogeneous granite surface. Rutherford Backscattering Spectrometry (RBS) technique was selected because it was demonstrated to be suitable to measure the diffusion of Au NPs of different size (from 2 nm to 250 nm) in a Spanish granite [5]. In previous work, the analyses were performed only on “white” minerals of granite, under conditions were both the NPs and the granite minerals were negatively charged. In the present study, the analyses are extended to other granite minerals, and trying to cover all possible particle / mineral electrostatic interactions.

EXPERIMENTAL SET-UP

Cerium oxide (CeO₂), hematite (Fe₂O₃) and gold (Au). (CeO₂) nanoparticles were selected. CeO₂ and Fe₂O₃ were supplied by AEA Technology and Au suspensions by BBInternational. Low mineralized granitic water, Na-HCO₃ type at pH 8.3 and with a conductivity of 282 µS/cm, was selected for the experiments to ensure stability.

The average particle size and stability were evaluated by Photon Correlation Spectroscopy (PCS) measurements. A Malvern Zetamaster was used to measure the zeta potential (ζ) as a function of the pH, to establish experimental conditions.

Figure 1A shows the zeta potential measured as a function of pH for all studied NPs as a function of pH. Au NPs of 20 and 40 nm are negatively charged over almost the whole pH range, with an isoelectric point near pH = 3.

CeO₂ showed positive zeta potential at initial pH (pH 3), with an initial particle size of 60 nm. At basic conditions zeta potential turned negative, with a value around -3 mV.

Fe₂O₃ NPs have an initial particle size of 125 nm, at pH 6, and zeta potential positive (maximum +50 mV) for pH < 7.5 and negative (-40 mV) at higher pH.

Granite from the FEBEX tunnel at the Grimsel Test Site Underground Laboratory (Switzerland) was selected [6].

In Figure 1B, the zeta potentials of the granite and its main minerals (feldspar, a mixture of quartz and plagioclase, biotite and muscovite) are plotted as function of the pH. Granite surface charge is, in average, negative at all pH. At acid pH, minerals with positive and negative charge coexisted, at acid-neutral conditions minerals showed neutral or negative charge and at basic conditions most granite minerals are negatively charged.

With this information, the experimental conditions for diffusion analyses were fixed. From the colloids, the evaluated cases were: (i) zero charge (Au at pH 3), (ii) low positive charge (CeO₂ and Fe₂O₃ at pH 4-5) (iii) high positive charge (Fe₂O₃ at pH 3, (iv) low negative charge (CeO₂ at pH 10) and (v) high negative charge (Au at pH 6). A summary of studied conditions is in Table 1.
For diffusion studies granite samples were cut into millimeter-sized slices with an average area of 1 cm². The granite surface was polished to standardize surface roughness. Granite slices, previously saturated in low mineralized granitic water, were immersed in the different suspensions at different pH conditions. Contact times ranged from 5 minutes to 4 days. Before RBS measurements, all the samples were cleaned with ethyl alcohol to avoid the presence of particles deposited on the surface [7].

The granite surfaces were analyzed with Rutherford Backscattering Spectrometry (RBS). RBS measurements were made with a HVEC 2.5 MeV Van de Graaff accelerator using 2.2 MeV α-particles with a scattering angle of 20º. All samples were covered with a carbon layer of about 100 Å to avoid electrostatic charge effects during ion beam radiation. Mean acquisition time was 45 minutes, with an accumulated charge around 100 μC. The typical areas analysed by RBS, upon our experimental conditions, are of 1 mm², so that single minerals can be analysed.

**RESULTS**

Figure 2 shows the RBS spectra of two granite minerals (biotite and quartz) after contact with CeO₂ colloids at pH 3. Only the spectra in those energies near the region of interest for Ce (1.8-2.0 MeV) are shown. The spectra simulations are also included. At pH 3, quartz minerals are negatively charged while biotite positively charged (Figure 1). In all RBS spectra obtained, the signal of Ce is clearly visible being the Ce peaks asymmetrical, presenting a tail pointing towards lower energies indicating that Ce colloids are penetrating in the granite, and therefore diffusing. However, diffusion length was longer in quartz or feldspar minerals most probably due to attractive interaction.

The same analyses were carried out in all considered cases, and in order to obtain diffusion lengths and diffusion coefficients on selected minerals spectra simulation was carried out as described in [5].

Table 1 presents a summary of diffusion coefficients measured by RBS on different granite minerals at different experimental conditions.

<table>
<thead>
<tr>
<th>Coll.</th>
<th>Size (nm)</th>
<th>pH</th>
<th>Colloid ζ (mV)</th>
<th>Mineral ζ (mV)</th>
<th>Da (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>20</td>
<td>6.2</td>
<td>-35 mV</td>
<td>Feldspar: -25 mV</td>
<td>(2.0 ± 0.1)·10⁻¹⁸</td>
</tr>
<tr>
<td>Au</td>
<td>20</td>
<td>6.2</td>
<td>-35 mV</td>
<td>Biotite: +15 mV</td>
<td>(4.7 ± 0.1)·10⁻¹⁸</td>
</tr>
<tr>
<td>Au</td>
<td>20</td>
<td>9.0</td>
<td>-30 mV</td>
<td>Feldspar: -25 mV</td>
<td>(1.0 ± 0.1)·10⁻¹⁸</td>
</tr>
<tr>
<td>Au</td>
<td>20</td>
<td>9.0</td>
<td>-30 mV</td>
<td>Biotite: +15 mV</td>
<td>(3.4 ± 0.1)·10⁻¹⁸</td>
</tr>
<tr>
<td>CeO₂</td>
<td>60</td>
<td>3.0</td>
<td>+8 mV</td>
<td>Quartz: -15 mV</td>
<td>(4.7 ± 0.1)·10⁻¹⁸</td>
</tr>
<tr>
<td>CeO₂</td>
<td>60</td>
<td>3.0</td>
<td>+8 mV</td>
<td>Feldspar: -15 mV</td>
<td>(4.3 ± 0.1)·10⁻¹⁸</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>60</td>
<td>4.5</td>
<td>+20 mV</td>
<td>Mica: -12 mV</td>
<td>(7.9 ± 0.5)·10⁻¹⁸</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>60</td>
<td>4.5</td>
<td>+20 mV</td>
<td>Quartz: -15 mV</td>
<td>(3.6 ± 0.5)·10⁻¹⁸</td>
</tr>
</tbody>
</table>

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