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Quantification of Au nanoparticles retention on a heterogeneous rock surface

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ABSTRACT

Colloid-mediated contaminant transport within geological media is still not fully understood, mainly because the mechanisms that lead to colloid retention onto the rock walls are not clear and are difficult to quantify.

This study presents an experimental methodology to quantify at a mineral scale colloid surface distribution coefficients (K_a) in a heterogeneous rock surface (granite). The retention of negatively charged Au nanoparticles of different size (2, 40 and 100 nm) was analyzed in static (batch) experiments. Two different pHs were used to account for different rock–colloid electrostatic interactions: the first one when the rock has some positively charged minerals and the nanoparticles are negatively charged (*favorable electrostatic attraction)* and the second case where all granite minerals and the Au nanoparticles are negatively charged (*unfavorable electrostatic attraction*).

The micro-Particle Induced X-Ray Emission (μPIXE) technique was used to visualize and quantify the colloid retention on the granite surface. Colloid surface distribution coefficients were measured on the main minerals composing the rock.

In the *favorable case*, higher K_a values were observed on the minerals bearing positive charge and a K_a dependence on the colloid size was observed. However, non-negligible K_a values were measured also on negatively charged minerals, without clear size dependence effects. The main mechanisms responsible for colloid retention in these unfavorable areas were analyzed. They were mostly related to higher porosity of certain minerals or to physical defects of the granite surface (roughness, grain boundaries).

The distribution coefficients obtained in this study can be used as input data for theoretical description of colloid transport in fractures.

1. Introduction

Colloids are particles of nanometer size (from 1 to 1000 nm) suspended in a fluid [1]. The high surface to volume ratio and their electrostatic charge make colloids very reactive to adsorb contaminants on their surface. If colloids are mobile, they can enhance contaminant transport in the environment [2–4].

The frame of this study is related to the possible colloid-mediated radionuclide (RN) transport in a geological repository for high-level radioactive waste (HLWR) emplaced in a granite massif [5,6]. RN themselves can exist in colloidal form (diameters <1–2 nm). Natural colloids, like iron oxides or clay colloids, can be naturally present in groundwater but also, colloids can be generated from the engineered barriers of the repository, for example bentonite clay colloids, that have hydrodynamic diameters of about 200 nm, can absorb RN [7]. The real impact of colloids in the RN migration within granite fractures in the repository case is still unclear [5].

In granite media, colloid transport mainly takes place by advection in conductive fractures being their transport significantly different to that of a solute. A fraction of colloids moved unretarded, compared to the water flow but in many cases, and depending on the experimental conditions, a colloid fraction is retained in the medium. Colloid retention was measured even under flow conditions and at pH conditions where both the whole rock surface and the colloids are negatively charged, so that repulsive forces must dominate and where higher retention was not expected [8,9]. In those cases, colloid deposition or colloid matrix diffusion alone could not either explain the observed retention [10,11]. The mechanisms that are retaining colloids in the fracture surface are not yet understood. Theoretical models investigated the relevance of the different retention mechanisms [12,13], even under the unfa-

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vorable case [14,15], but the lack of experimental data obtained in realistic conditions still prevents a reliable validation of theoretical predictions.

Colloid deposition and retention on surfaces have been deeply studied, by different batch or column experiments, usually in simplified materials with well-defined geometry [16–18]. Amongst many physical and chemical properties [19,20], the effects of the fluid flow [21,22], the particle size [16,23,24], the surface roughness [25,26], electrostatic charges [27–31] on colloid retention [32,33] were evaluated. Most studies were performed with particles larger than 1 μm but less with nanoparticles, and the properties of materials change significantly as their size approaches the nanoscale. In particular, no quantitative study on colloid/granite interactions is available. In a former study, we qualitatively analyze colloid/granite surface interactions with different type of colloids [34], but further efforts on quantification were still required.

The aim of this study is to quantify the retention of colloid particles in the nanometer size, on a heterogeneous granite surface. Analyses are carried out at mineral scale, since a nanoparticle would not be affected by the physicochemical conditions of the average granite surface, but by the specific conditions of a certain mineral, grain boundary, roughness or defect [35]. To quantify the retention of Au negatively charged nanoparticles, two pH conditions were considered in terms of electrostatic interactions: attractive particle/rock electrostatic interactions (*favorable case, pH 5*) or repulsive particle/rock electrostatic interactions (*unfavorable case, pH 9.5*). It is considered that a mineral is positively charge (pH_{pzc}) when the pH is lower that the point of zero charge and negatively charged when the pH is higher than pH_{pzc}. Retention experiments are performed under static conditions.

The preferential colloid retention onto minerals is analyzed by the nuclear ion beam technique μPIXE (micro-Particle Induced X-Ray Emission) [36,37].

In this study, gold colloids of different diameters, in the nanometer range, were selected for the study. Au colloids are stable and Au is easily identified within granite with μPIXE [11]. In addition, their availability in different mono-disperse size distributions allows additionally analyzing the colloid size effects on the retention. Other colloids, like for example bentonite colloids that can be generated in a HLWR, could not be detected inside granite by μPIXE because of their high Si and Al content [38]. Anyhow, Au colloids have equivalent charge as the bentonite colloids [34].

Colloid retention on the fracture walls can be described by an average surface distribution of colloids (K_a in m) [39]. Therefore, colloid distribution coefficients on the main minerals composing the granite (quartz, plagioclase, K-feldspar, biotite, epidote, chlorite and ilmenite) are evaluated, under both the *favorable* and *unfavorable* cases for the retention, previously described.

Table 1
Summary of the main characteristics of the “as received” gold colloids.

Size (nm)	Particles/ml	Concentration (ppm)	Conductivity (μS/cm)	pH
2	15E+13	12.1 ± 0.2	8.0 ± 0.2	6.19
40	9E+10	58.2 ± 0.2	8.0 ± 0.2	6.16
100	5.6E+9	56.6 ± 0.2	9.0 ± 0.2	5.46

2. Materials and methods

2.1. Materials characterization

2.1.1. Gold colloids

Commercial gold nanoparticles of 2, 40 and 100 nm (BBInternational) were selected for the study. These nanoparticles are obtained from $HAuCl_4$ by gold reduction with the negative charge coming from dichlorogold (I) ions adsorbed on the colloids outer surface [40]. As indicated by the supplier, the colloids were suspended in pure water and only containing a residual gold chloride concentration of 0.001%. Assuming this gold chloride concentration in solution, and the measured conductivity of 8 μS/cm (Table 1), an ionic strength lower than 10^{-4} M is calculated. This ionic strength and both pHs ensures gold colloid stability [34]. The concentration and main characteristics of the “as received” colloid suspensions are included in Table 1. The surface charge of the colloid particles was evaluated by zeta potential measurements at different pH. The zeta potential (ζ) measurements were performed in diluted (1:25) suspensions with a Malvern Zetamaster equipped with a 5 mW He–Ne laser (λ = 633 nm).

Fig. 1A shows the zeta potential measurements of the Au colloids as a function of pH. Gold colloids are negatively charged over almost the whole pH range, with an isoelectric point near pH 3, responsible for the rapid coagulation near this pH. The zeta potential values measured for the bentonite clay colloids (generated in a HLWR environment) are also plotted in Fig. 1A, to point out that they have similar charge.

2.1.2. Granite

The selected granite comes from the FEBEX site located in the underground laboratory of the Grimsel Test Site (Switzerland) [41]. The mineral composition of this granite (in %) and their structural formulas are presented in Table 2.

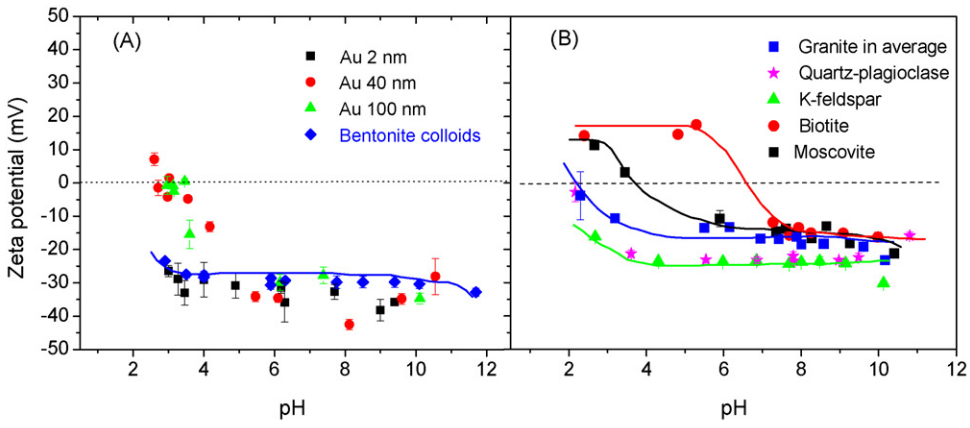

Fig. 1. (A) Zeta potential of the Au colloids of 2, 40 and 100 nm as function of the pH. The zeta potential measurements of bentonite colloids, of interest in a HLWR, are presented for comparison. (B) Zeta potential measured for crushed granite and for different minerals composing it (muscovite, biotite, feldspar and a mixture of quartz-plagioclase) as function of the pH.