



## **BELBaR**

(Contract Number: FP7 295487)

# **Progress report on microscale investigations on colloid mobility controlling processes**

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Reporting period: **01/03/12 – 01/06/13**

**Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research & Training Activities (2007-2011)**

Date of issue of this report: **01/06/13**

Start date of project: **01/03/12**

Duration: **48** Months

Dissemination Level		
<b>PU</b>	Public	<input checked="" type="checkbox"/>
<b>RE</b>	Restricted to a group specified by the partners of the BELBaR project	<input type="checkbox"/>
<b>CO</b>	Confidential, only for partners of the BELBaR project	<input type="checkbox"/>

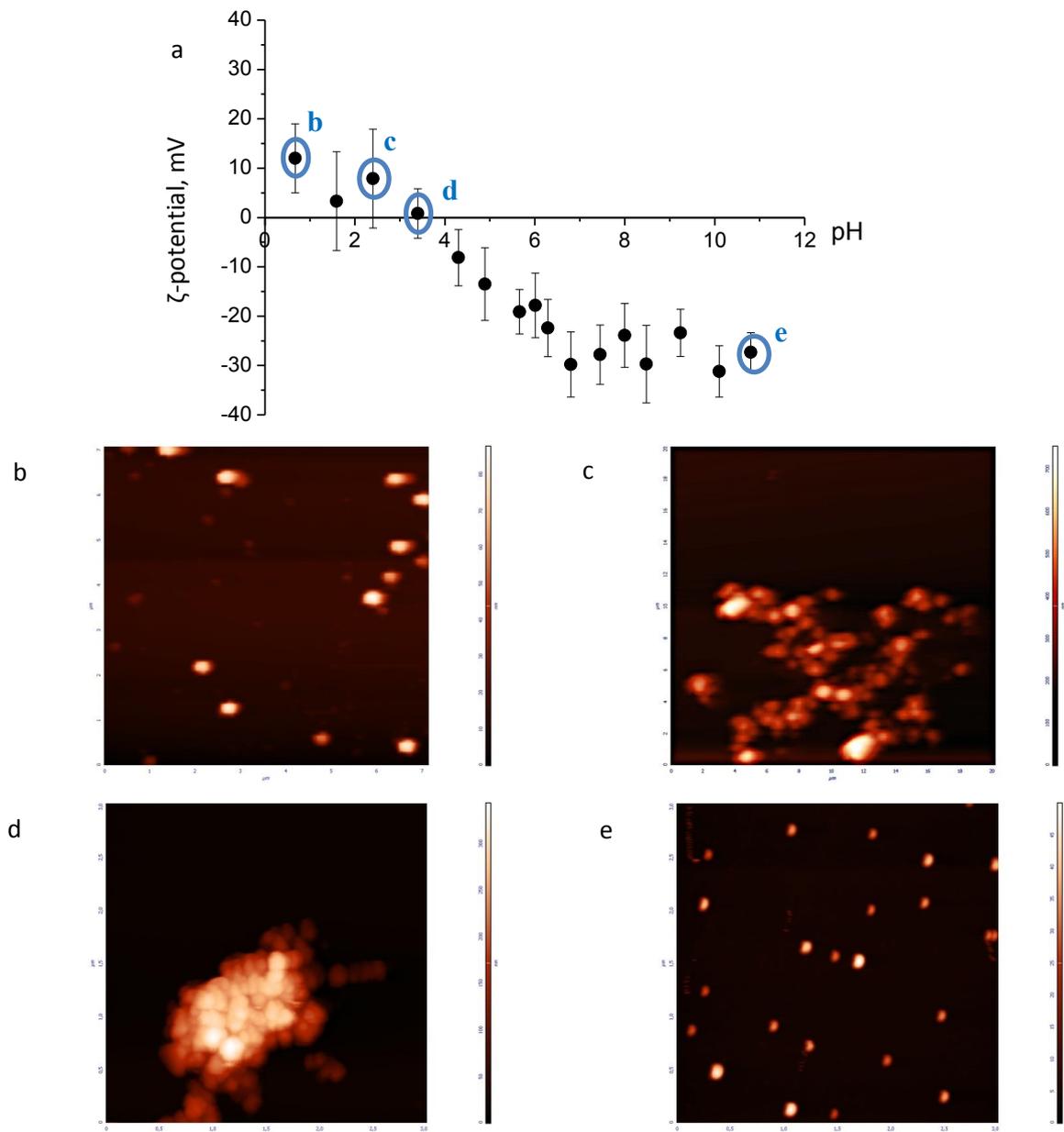
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# 1 Microscale investigation on colloid mobility controlling processes: MSU contribution

MSU analyzed the microscale characteristics of artificial (silica and hematite) colloids in dependence on electrolyte and radionuclide concentration.

Hematite was synthesized using forced hydrolysis reaction. Absence of impurities was approved by XRD and Mössbauer spectroscopy. The  $\zeta$ -potential dependence on pH was studied for pure hematite colloids (Fig. 1a). The isoelectric point was found to be  $\text{pH}_i = 3.4$  which is lower than known values for hematite ( $\sim 8$ ) probably due to specific adsorption of anions (background electrolyte 0.1 M  $\text{NaClO}_4$ ).

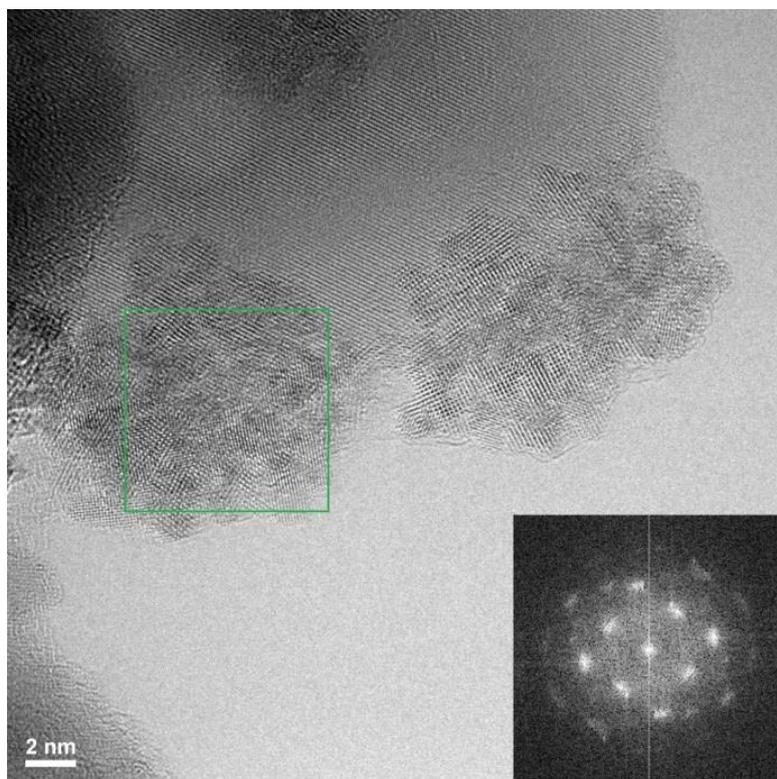


**Fig 1: (a) The  $\zeta$ -potential dependence on pH of hematite colloids; (b), (c), (d) и (e) AFM images of hematite suspensions at different pH values.**

Investigated hematite suspensions at different pH values were characterised by atomic force microscopy (AFM), that allows to obtain pictures of particles and aggregates without changing their structure. AFM images show aggregation of colloidal particles at different pH (Fig. 1b,c,d,e). Particles are separated for suspension with absolute value of  $\zeta$ -potential  $> 10$ . Decrease of the  $\zeta$ -potential values down to zero results in aggregation of hematite particles, that is clearly seen from AFM images.

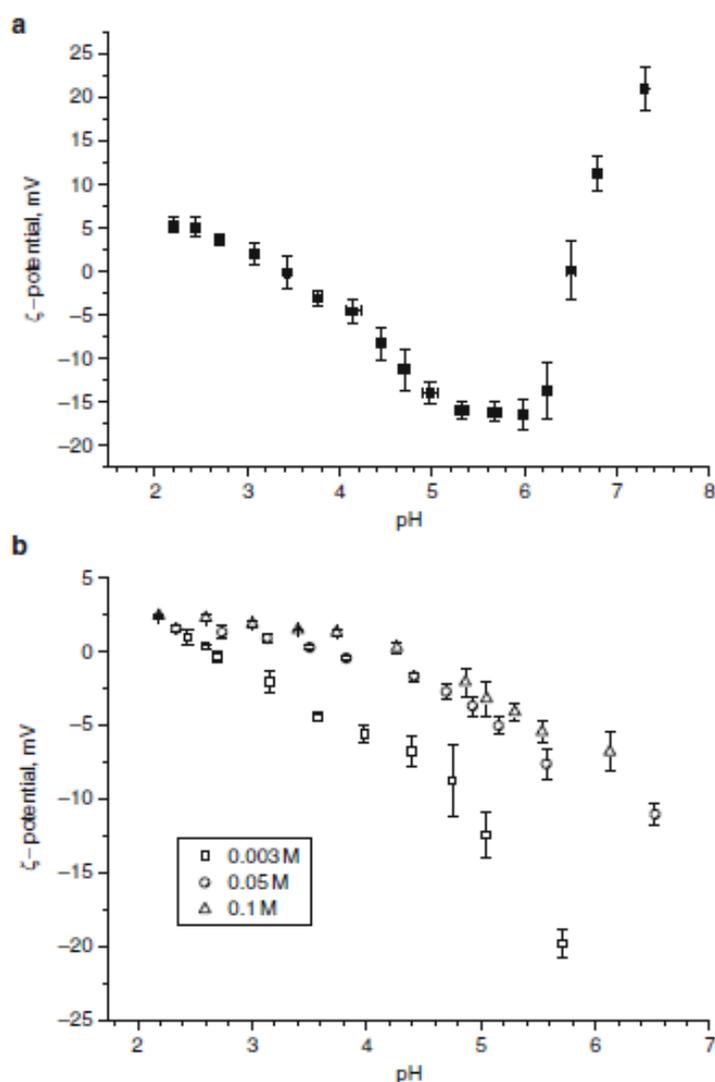
Sorption experiments of plutonium onto hematite particles were done using Pu(VI) as initial oxidation state since both Pu(VI) and Pu(V) are quite soluble compared to Pu(IV). For all the sorption experiments the hematite suspension was prepared using 0.1 M NaClO<sub>4</sub> as a background electrolyte. The hematite suspension was sustained during several days in the background electrolyte solution prior to adding the Pu. The hematite suspensions equilibrated with Pu ([Pu]<sub>tot</sub>=10<sup>-6</sup> M) during 6 months were examined by XAFS and HRTEM. The pH and Eh was controlled periodically and small adjustments of pH were done by adding few drops of diluted NaOH and HClO<sub>4</sub>.

It was observed that interaction of Pu(VI) with hematite colloids lead to the formation of Pu(IV) nanocolloids [2]. This effect is clearly demonstrated in this study by HRTEM and EXAFS at the Pu total concentration of ca. 10<sup>-6</sup> M. This mechanism remains feasible even at much lower concentrations, e.g. 10<sup>-9</sup> M. While the determination of Pu speciation by EXAFS is limited to plutonium concentrations higher than ca. 10<sup>-6</sup> M, HRTEM could be successful if the Pu is in nanoparticulate form (Fig. 2). Thus hematite colloids can be modified not only by surface complexation with radionuclide, but also by deposition of radionuclide bearing nanoparticles.



**Fig. 2: HRTEM images of PuO<sub>2+x</sub>·nH<sub>2</sub>O nanoparticles, which are formed as a result of the interaction of Pu(VI) (initial oxidation state) with hematite and a typical FFT from these particles.**

The silica colloids were synthesized by the Stöber reaction based on hydrolysis of tetraethoxysilane, TEOS, in the presence of ammonia in ethanol. This reaction enables synthesis of spherical colloidal silica particles with a narrow size distribution. For the silica suspensions the  $\zeta$ -potential dependence on pH was studied in the absence and presence of uranium (VI) [1]. At pH <6, where uranium sorption can be neglected, the decrease of the  $\zeta$ -potential with pH follows the same trend as for pure silica colloids (Fig. 3). In contrast, at pH >6, when the maximum uranium sorption is observed, the  $\zeta$ -potential sharply increases and reaches positive values at pH 6.5. This trend of the  $\zeta$ -potential dependence with pH is controlled by modification of the silica surface properties due to uranium sorption. This important observation indicates an increase of silica colloid stability at neutral pH and therefore an increase in the potential role of colloidal facilitated transport of elements such as uranium.



**Fig. 3. Measured pH dependencies of  $\zeta$ -potential for silica colloids (a) in presence of U(VI) at total concentration  $10^{-5}$  M, (b) in absence of U(VI), at various  $\text{NaClO}_4$  concentrations in suspension [1].**

Similar behaviour was observed for  $\text{TiO}_2$  colloidal particles in the presence of europium (Fig. 4). Increase of Eu concentration at pH > 5 leads to higher values of  $\zeta$ -potential of the particles, that is consistent with pH-dependence of europium sorption.

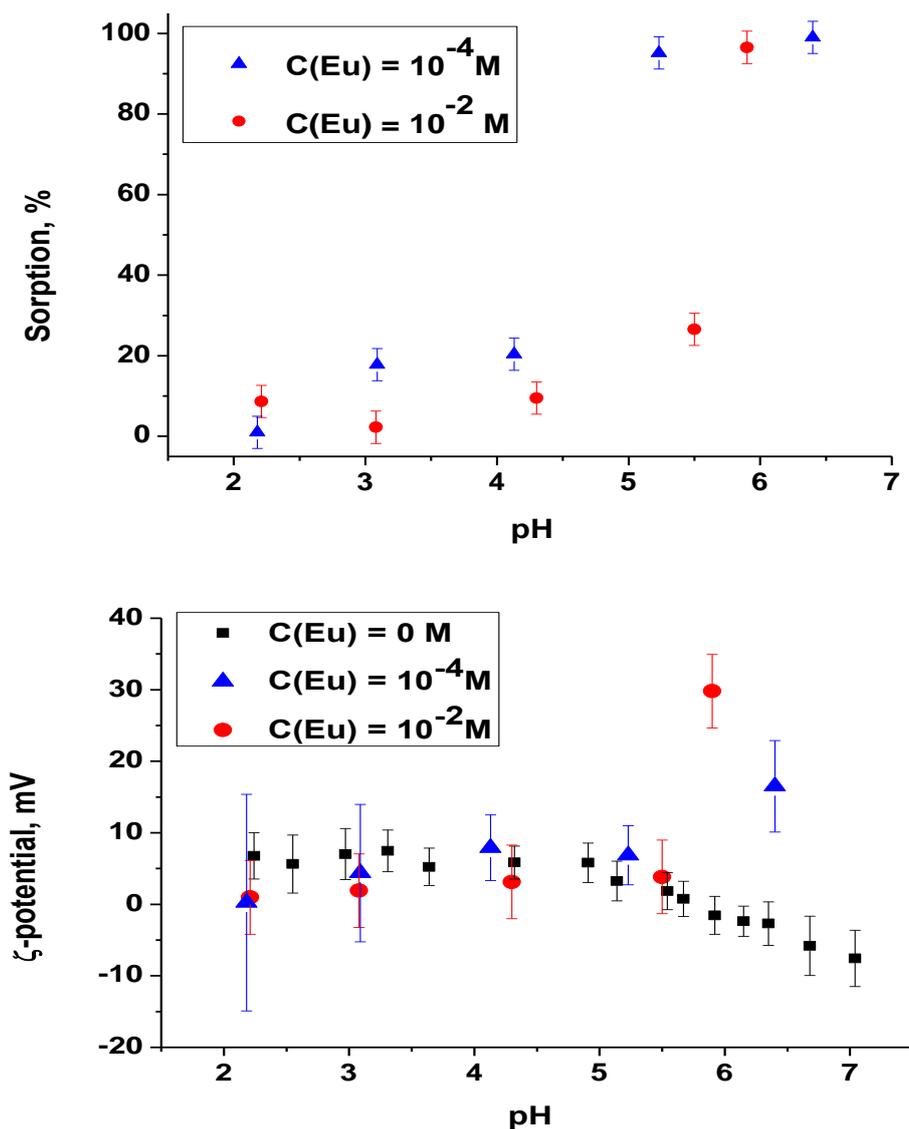


Fig. 4: Sorption (top) and  $\zeta$ -potential (bottom) dependence on pH for  $\text{TiO}_2$  colloidal particles in presence of Eu.

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2. Romanchuk A.Yu., Kalmykov S.N. et al.  $\text{PuO}_{2+x} \cdot n\text{H}_2\text{O}$  crystalline nanoparticles formation upon Pu(V,VI) sorption onto hematite (**2013**, submitted to GCA).

## **2 The influence of mineral/fracture surface roughness and Eu concentration on colloid retention probed by atomic force microscopy (AFM) colloid probe technique: KIT-INE contribution**

Understanding the sorption processes at the interface of colloids and mineral surfaces where both the colloids and mineral surfaces are negatively charged is important to answer key questions related to transport and retardation of colloids in the nuclear waste repository [1-3]. In the current study the sorption of colloids onto minerals as a function of surface heterogeneity and metal ion (Eu(III)) concentration is studied. The colloid sorption results obtained from flow-through experiments are verified by measuring the actual forces applying colloid probe technique (Atomic Force Microscope (AFM)).

Colloidal suspension of carboxylated polystyrene particle (latex, diameter =  $1000 \pm 25$  nm and concentration =  $48 \times 10^6$  particles / mL, NaCl =  $10^{-3}$  M) was exposed to the main mineral constituents of granodiorite surface (quartz, plagioclase, K-feldspar, biotite) possessing varying surface roughness in a fluid cell (velocity =  $4.7 \times 10^{-7}$  m / sec) for 1 h (at pH = 5). Vertical Scanning Interferometry (VSI) is applied for surface topography characterization and colloid quantification. AFM cantilevers modified with carboxylated latex colloids were used to obtain force-volume measurements under the similar chemical conditions. The data from VSI and AFM was processed using SPIP software from image metrology, Denmark.

At pH=5, all minerals are negatively charged leading to unfavorable deposition conditions. At Eu(III) = 0 M and for a surface roughness range of 250 nm, colloid deposition is ranked as quartz  $\approx$  K-feldspar > plagioclase > biotite while, at high Eu concentrations ( $10^{-6}$  M) the order of sorption reactivity becomes quartz > plagioclase > K-feldspar > biotite. In general, increasing Eu(III) concentration from zero to  $10^{-6}$  M increased the colloid deposition rate. The increase is by a factor of 4.5 for plagioclase, 1.8 for biotite, 2.7 for K-feldspar and 3.4 for quartz (Fig. 5a). Colloid deposition efficiencies on feldspars and quartz minerals were nearly 2 to 4 times higher than biotite. From the measured forces (snap-in and adhesion) using colloid probe technique, the adhesion forces explain well the observed sorption results better than snap-in forces. Interestingly, the force-volume measurements along the rough mineral surfaces predict a higher adhesion forces for flat surface sections compared to pits or positive asperities towards colloid retention highlighting the differences in reactivity with respect to surface heterogeneity (Fig. 5b). The differences in measured forces could be due to the decreased local contact area at the interface of colloid-rough surface (Fig. 5c) or differences in the distribution of Eu on rock surface with respect to physical heterogeneity.

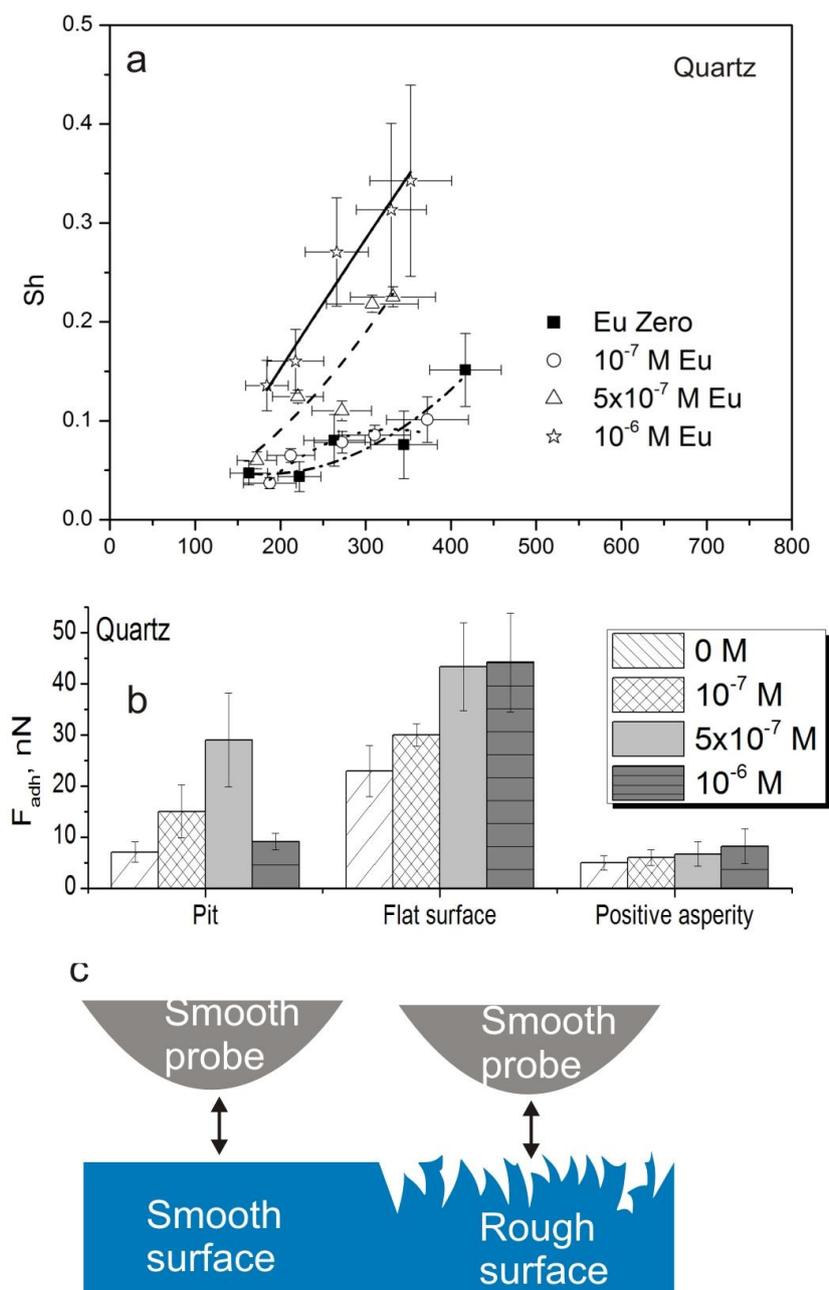
Further details on this research can be found in the references listed below.

### **ACKNOWLEDGEMENT**

This study was partly supported by a GEOTECHNOLOGIEN Grant No. 03G0719A (University of Göttingen, Germany). Financial support by the Federal Ministry of Economics and Technology (BMW) under the joint research project "KOLLORADO 2" is gratefully acknowledged by KIT-INE.

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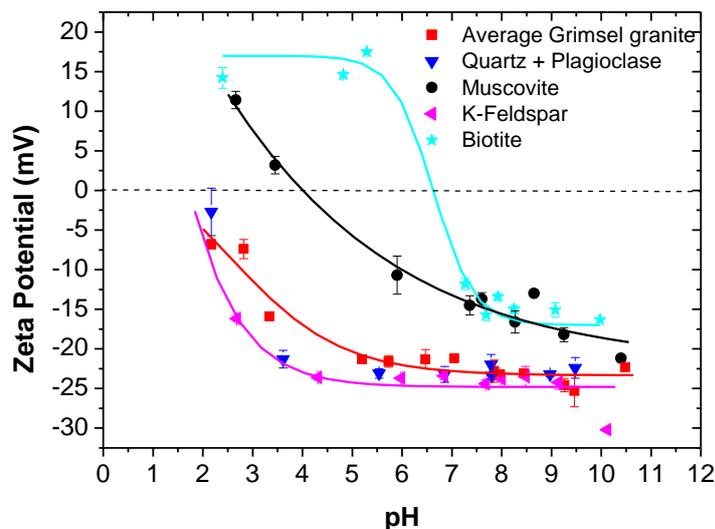


**Fig. 5:** a. colloid deposition density ( $Sh$ ) as a function of surface roughness and  $[Eu(III)]$  on quartz substrate, b. adhesion forces on quartz surface at varying  $[Eu(III)]$  as a function of surface heterogeneity, c. scheme to explain the reduced local contact area between colloid and surface with an increase in the surface roughness.

### 3 Progress report on microscale investigations on colloid mobility controlling processes: CIEMAT contribution

CIEMAT analyzed the transport behavior of artificial (gold and latex) and natural (smectite) colloids within artificial fractures in natural crystalline rock (GRIMSEL) to start analyzing filtration phenomena (Albarran et al 2013) and to relate macroscopic observation to mechanisms at the microscale. The colloids selected for transport experiments presented different size, shape, density and surface charge: the effects of these parameters on their transport and retention in the fractures were evaluated in conjunction with the effects of the hydrodynamic characteristics of the system (water velocity/residence time in the fracture and fracture width (Albarran et al 2013).

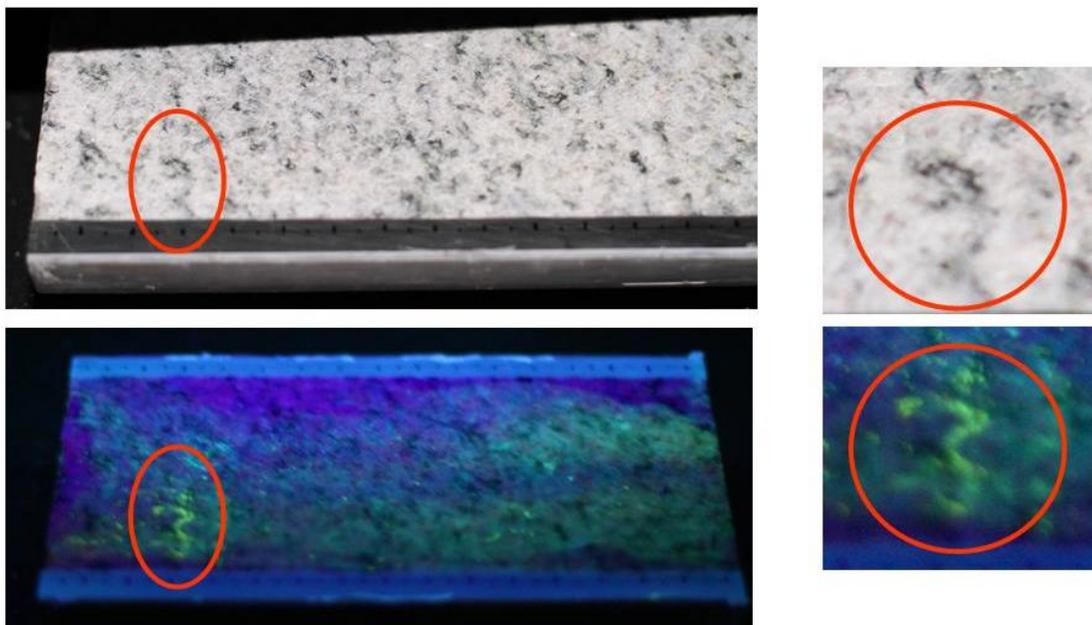
Alonso et al. (2009) measured the zeta potential of a Grimsel granodiorite, and its main composing minerals, that can be appreciated in Figure 6. It showed that the overall charge of the rock in neutral to alkaline conditions is also negative (with values from  $-15$  to  $-25$  mV). Under the chemical conditions used for transport experiments (pH between 7 and 10 and ionic strength  $5 \cdot 10^{-4}$  M in  $\text{NaClO}_4$ ) all the colloids presented negative charge, with zeta potential values ranging from  $-70$  mV to  $-30$  mV approximately, with the highest values corresponding to latex particles.



**Fig. 6: 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.**

Thus, colloid transport in the fracture occurs under electrostatic conditions unfavorable to attachment, and in spite of clear exclusion effects observed, colloids were retained on the fracture surface above all under low water flow rates. Under similar water velocities, the recovery of smectite colloids was always higher than that of latex and gold colloids, most probably due to the different morphology of the particles.

To evidence how retention of colloids on the fracture surface occurred, a post-mortem analysis of the fracture surfaces was carried out. Figure 7 shows the column opened after tests with fluorescent colloids. Before starting transport test in this column, the fracture surface was photographed and visualized under an ultraviolet light ( $\lambda = 254$  or  $366$  nm), to detect possible region with natural fluorescence. In general, apart from very small luminescent spots, probably related to uranium minerals, these surfaces did not present fluorescence. After the transport tests, the presence of colloids is perfectly visible under the ultraviolet light. In particular, the largest colloids (500 nm) can be better distinguished amongst the others for their strong yellow color compared to the light-green color of 30 and 150 nm colloids. Thus, the deposition of colloids on the granite surface was clearly visible and their retention in the fracture proven. Clearly, colloids were not evenly distributed all over the surface: less fluorescence was detected in the center of the fracture (probably the zone of the highest flow) and the most intense fluorescence was detected in regions with surface defects like microfractures, as that shown in the enlarged picture at the right side of the figure.



**Fig. 7: Granite column under natural (above) and ultraviolet (below) light. A detail marked with the red circle, indicating a granite microfracture, is amplified on the right side.**

Colloid retention was observed mainly in zone of the rock with defects, micro-fractures and grain boundaries and increased significantly as the water flow rate decreased. The retention behavior observed could not be totally explained considering only sedimentation and Brownian motion effects.

Furthermore, a specific link between colloids deposited on the surface and particular minerals was not observed. This is in agreement with previous studies performed by Alonso et al. (2009) and Chinju et al. (2001). In Alonso et al., (2009) the surface retention of negatively charged Au colloids was analyzed by micro-Particle Induced X-Ray analyses on the heterogeneous granite surface, at mineral micro-scale. Studies were carried out both under *favorable* (at pH 5 where some minerals

are positively charge) and *unfavourable* cases (at pH 9 where the whole granite surface is negatively charged), in terms of electrostatic interactions. Higher distribution coefficients were measured, in the favorable case on attractive minerals, being dependant on the colloid size. However, non-negligible distribution coefficients were measured on minerals which showed the same charge of colloids. Colloid retention on granite was found to be strongly dependent on small scale chemical effects, roughness or non-uniform distribution of charge sites (Alonso et al., 2009).

Albarran et al. (2011) analyzed the surface of a similar fracture after transport experiments with smectite colloids, and also observed their non-homogenous deposition over the surface. Colloid retention was mainly dependent on the existence of surface defects, which basically determine the roughness of the rock. Shellemberg and Logan (2002) also stated that roughness at a molecular scale and heterogeneities (structural of charge) may represent very important factors in the deposit of colloid onto surfaces (Darbha et al. 2012, 2012b).

Microscopic heterogeneities as dislocation, defects or grain boundaries are important for microscopic entities as colloids. Deposit of colloid may occur in these active zones, even when, in mean the surface characteristic are not favorable for particle retention (Dabros et al, 1993). Increase of local concentration in these active zones may also produce additional ripening phenomena that also would favor the retention in the fracture (Camesano et al 1999).

## CONCLUSIONS

The experimental retention behavior presented by all the colloids cannot be satisfactorily explained considering the characteristic of colloids (charge and size) and the main mechanisms affecting deposition in a colloidal system (Brownian diffusion and sedimentation). The main mechanism that seems triggering deposition processes is the existence of roughness and heterogeneities at a molecular-micro scale.

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