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(Contract Number: 295487)

DELIVERABLE (D-N°:4.5)

KIT-INE Progress report on colloid stability and DOC effect

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Reporting period: 01/09/13 – 28/02/15

Date of issue of this report: **31/05/14**

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

Duration: 48 Months

Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research & Training Activities (2007-2011)		
Dissemination Level		
PU	Public	PU
RE	Restricted to a group specified by the partners of the BELBaR project	
CO	Confidential, only for partners of the BELBaR project	

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Starting point

The stability of clay colloid is one of the key uncertainty in the long-term performance assessment of a radioactive waste disposal. This property is strongly site specific as being driven by the groundwater “geo”chemistry such as the salinity and the pH which governs the edge charge.

According to our previous work [1], performed over a 3 years period, the clay colloids undergo a continuous agglomeration process even in natural ground water where conditions were first thought to be ideal for clay colloid stabilization: high pH (8-9) under low ionic strength conditions. The water chemistry and mainly the Ca^{2+} concentration were thought to determine the colloid size distribution.

The aim of this additional experimental work program is to examine in more details the agglomeration process and its reason.

Experimental approach

The MX80 bentonite colloid stability is examined systematically under different chemical conditions, starting from a delaminated bentonite clay suspension.

The raw material is first sieved and the fraction $< 63 \mu\text{m}$ is used. Clay suspensions (6 x 1L) are prepared at 10 g/ L in LiCl 1M. After 1 week, the suspensions are centrifuged, rinsed and resuspended in 6 different electrolytes (aqueous media) simulating a natural waters at low ionic strength ($\text{IS} = 1.3 \cdot 10^{-3} \text{ M}$). The rinsing electrolytes consist in 1) MQ at pH 5.7, 2) NaCl $1.3 \cdot 10^{-3} \text{ M}$ at pH ~ 5.7 , 3) CaCl_2 $0.433 \cdot 10^{-3} \text{ M}$ at pH ~ 5.7 ; 4) NaHCO_3 10^{-3} M at pH ~ 8.4 , 5) a SGW at pH ~ 8.5 and 6) a SGW at pH ~ 5 .

The acronym SGW is used for Synthetic Ground Water as it is supposed to simulate a glacial melt water with Na^+ , Ca^{2+} , SO_4^{2-} , Cl^- , F^- , HCO_3^- and trace of Si at 2 different pHs.

The colloidal suspensions obtained after the fourth centrifugation/rinsing/re-suspension step become the colloidal clay stock suspensions. The results of the first analysis (obtained from IC, ICP-OES and PCS) are summarized in Table 1.

Table 1: Characterization of 6 clay colloidal stock suspensions.

Electrolyte	4 th [Colloids] supernatant	4 th pH supernatant	Size range nm (PCS)
MQ	1.95 g.L	9.9	270-300
NaCl 1.3 10 M	1.38 g.L	9.9	240-300
CaCl ₂ 0.433 10 M	1.56 g.L	9.9	
NaHCO ₃ 10 M	1.59 g.L	9.6	270-310
SGW pH ~ 8.5	0.92 g.L	9.3	290-350
SGW ~ pH 5	0.87 g.L	9.7	270-320

It appears clearly that one of the cation present in the SGW has strongly influenced the colloidal production.

A great number of batch samples have then been prepared using these 6 colloidal clay suspensions (Picture 1). They were all diluted at different concentration (1, 5, 10 and 100 mg/L) in each of the 6 pre-cited electrolytes to study the colloid stability over a long time period, at least up to the end of the project and beyond.



Picture 1: Batch samples prepared for the long term stability study.

A set of sample at 10 mg/L colloids concentration contains a tetravalent actinide element (Th(IV) at 10^{-8} M, especially for a reversibility study) and another set, Fe⁰ (~2,5-3 mg). The influence of organic matter (OM) is examined in parallel exactly under the same conditions by adding 10 mg/L fulvic acids (FA-573) before the dilution in each of the precited electrolytes.

The samples have been prepared, as seen, and are now ready for further characterization (PCS, AsFIFFF/UV/ICPMS, ...). They are stored in the laboratory (at ~ 21-22°C) but preserved from the light. The first intensive analysis is planned in 1 year, which means the samples will be 2 years old. The results will be always compared with those obtained from freshly prepared samples.

In addition to this slow coagulation study, the fast coagulation rates will be determined in presence or not of OM (see deliverable D4.6).

Management

An undergraduate student (Mrs Y. Heyrich) has gained a first experience in a laboratory by preparing the different suspensions and by receiving an introduction to the different analytical techniques used during her work (03/06/13-26/07/13).

Reference

[1] Bouby, M.; Geckeis, H.; Lützenkirchen, J.; Mihai, S.; Schäfer, T. (2011) Interaction of bentonite colloids with Cs, Eu, Th and U in presence of humic acid: a Flow Field-Flow Fractionation study. *Geochimica and Cosmochimica Acta*, 75(13), p3866-3880 and in the corresponding supplementary data file, <http://dx.doi.org/10.1016/j.gca.2011.04.015>.