Karlsruhe Institute of Technology

Institute for Nuclear Waste Disposal (INE),
P.O Box 3640, D-76021 Karlsruhe, Germany
*: corresponding author, muriel.bouby@kit.edu

WP4

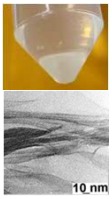
Influence of organic matter (fulvic acids, FA) on the (long term) stability of clay colloids prepared under different chemical conditions

M. Bouby*, Y. Heyrich, S. Heck, S. Hilpp, T. Schäfer

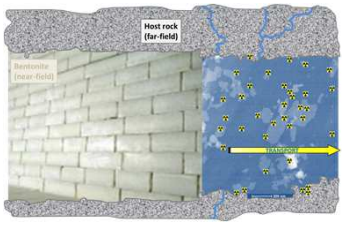
Introduction

• *Bentonite is envisaged as a suitable hostrock / backfill material in most designs of high level radioactive waste repositories*

•*In contact with water, a GEL will form which can take a SOL character under specific conditions (ex: fresh age ice waters) resulting in the bentonite barrier erosion and thus a loss of its integrity*



• *The clay colloidal release may impact the radionuclide (RNs) dissemination in the geosphere, IF . . . . . .*



.... The clay colloids are proved to be STABLE ?!

Aim of this work

✓ *The colloid stability depends on chemical parameters like the pH, the ionic strength (IS), the ionic composition and the presence of natural (in)organic complexing agents (like humic (HA) or fulvic (FA) acids)*

✓ *Agglomeration of bentonite clay colloids was already reported even under conditions (i.e. high pH, low IS) initially thought to be ideal for a clay colloid stabilisation [Bouby et al., GCA, 2011, 75(13), 3866]*

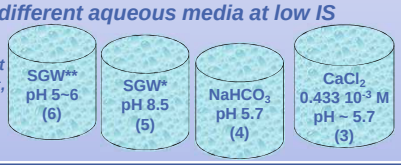
These additional experiments performed in the frame of the BelBar project (WP4) aim to examine in more details the effects on the long-term stability of clay colloids of :
1) the presence of specific ions (CO_3^{2-}, Ca^{2+}, Na^+,...)
2) the FA addition, as a potential source of dissolved organic carbon (DOC)

Preparation of clay colloidal stock suspensions

- *MX80 (Volclay)*
- *Sieving (Fraction < 63 µm used)*
- *10 g in 1L LiCl 1 M*
- *Contac time : 1 week under slow stirring + 4 days*

- *Repartition in tubes followed by*
- *4 extraction cycles consisting on*
  - *a centrifugation at 35' at 3500 rpm*
  - *a removal of the supernatant*
  - *the re-suspension of the clay solid/ gel-like residues in 6 different aqueous media at low IS*

**:SGW: Synthetic Ground Water, glacial melt water type, containing Na^+, Ca^{2+}, SO_4^{2-}, Cl^-, F^-, HCO_3^-, trace of Si*
***: like SGW, without HCO_3^-*



✓ **The 6 supernatants collected at the end of the 4th cycles constitute the 6 clay colloidal stock suspensions**

First characterizations: IC, ICP/OES, pH, PCS

Aqueous medium	[Colloids] g.L^{-1}	pH	Size range nm (PCS)
Ultra pure water	1.95	9.9	270-300
NaCl 1.3 10^{-3} M	1.38	9.9	240-300
$CaCl_2$ 0.433 10^{-3} M	1.56	9.9	240-350
$NaHCO_3$ 10^{-3} M	1.59	9.6	270-310
SGW pH ~ 8.5	0.92	9.3	290-350
SGW ~ pH 5-6	0.87	9.7	270-320

Table 1: First characterization of the 6 clay colloidal stock suspensions, i.e. the 4th supernatants

✓ **[Si]/[Al] and [Al]/[Mg] ratios suggest the release of clay colloids**

✓ **Their size is in the range expected, further investigations are necessary to check the presence of smaller-sized clay particles**

✓ **The composition of the SGW strongly decreases the clay colloid production**

Fast coagulation experiments

- *Dilution of the 6 clay colloidal stock suspensions in the corresponding aqueous media: [Colloids] = 10 mg.L^{-1}*
- *With or without FA (2.5 mg.L^{-1})*
- *IS: 0.1 M, 1 M, 3 M with NaCl, $CaCl_2$, $MgCl_2$*
- *PCS studies: evolution of the mean hydrodynamic diameter*

✓ **Whatever the initial aqueous media in which the clay colloids are suspended, they present the same coagulation behavior at moderate to high (0.1 M, 1 M, 3 M) IS in NaCl, $CaCl_2$ or $MgCl_2$ electrolyte**

✓ **In 0.1 M NaCl IS, the coagulation rate slows down**

✓ **The presence of FA only prevents or slows down the clay coagulation in 0.1 M NaCl but in none of the other conditions tested.**

In view of the literature, the results seem independent of the origin of the clay or the organic matter and can be generalized

Long term stability study

- *Dilution of the 6 clay colloidal stock suspensions in the corresponding aqueous media ...*
- *... Containing or not additional FA [2.5 mg.L^{-1}]*
  - ✓ *[Colloids]: 1, 5, 10, 100 mg.L^{-1}*
- *12 samples available for each set of conditions, stored at room temperature (~21-22°C), preserved from light*
- *Samples are now 33 months old*

First analysis of 2.5 years old samples from aqueous media (6) with FA: promissing!

✓ **pH constant: 6.4 ± 0.1**
✓ **Size (Ø, PCS_I): 205 ± 16 nm, after shaking: > 310 nm**
✓ **Colloid concentration gradient**

Under the present experimental conditions, i. e. glacial melt water at quasi-neutral pH, the clay colloids undergo a slow agglomeration process even in presence of organic matter

These results have received funding from the European Atomic Energy Community's (EURATOM) 7th Framework Programme (FP7/2007-2011) under the grant agreement No. 295487, the BELBaR project.