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## **DELIVERABLE (D-N°: D4.11)**

Final report on experimental results on clay colloid stability  
WP4

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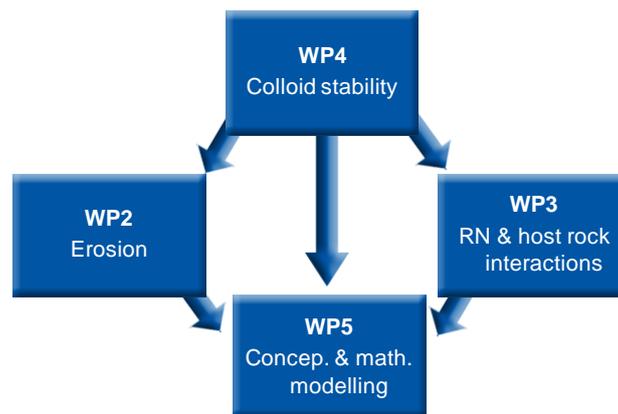
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## Introduction

The possible erosion of the bentonite barrier of a high-level waste repository leading to the generation of colloidal particles was investigated for two main reasons:

- the long-term integrity of the bentonite barrier (erosion proc. Work Package 2)
- the role of clay colloids in radionuclide transport (transport proc. Work Package 3)

Both the erodibility of the clay barrier and colloid transport in the environment are strictly related to the water chemistry and also to the intrinsic properties of colloids and their stability behaviour. Thus, the analysis of the chemical conditions that make colloidal system stable or unstable is important because the conditions that favour colloid stability are also expected to favour colloid transport and erosion processes. In general, a colloidal system is considered as *stable*, if suspended particles do not undergo coagulation at least during the observation time. Because colloid stability depends on the chemistry of the aqueous environment, the stability studies analyse whether or not clay colloids aggregate depending on several chemical and physical parameters, such as pH, ionic strength, temperature, presence of different inorganic ions and organic ligands, amongst other factors. It is also important to understand what intrinsic physico-chemical properties of the bentonite may affect the stability of colloids. So, the knowledge about the stability of clay colloids in the site-specific host rock conditions is important for assessments of long-term performance of radioactive waste repositories. Work package 4 “*Colloid stability*” (WP4) was therefore integrated to the project structure as follows (see Figure 1).



**Figure 1: Link among individual WPs.**

Based on the analysis in WP1 the main crucial issues for WP4 were identified at the beginning of the project (Figure 2). Many coagulation studies of colloidal clay dispersions were performed under different geochemical conditions last decades (e.g. summary can be found in Lagaly, 2006). However a less attention was given to find the main reason for different behaviour of different clays. In this project some insight was done concerning the trend or correlation between the bentonites characteristics and its stability.

The coagulation of colloids is a fast process, if the conditions are favourable for coagulation (e.g. the concentration of some cation(s) is above critical coagulation concentration for given clay dispersion - CCC). But if we are at the boundary, close to conditions which are favourable for clay colloids coagulation, the aggregation process can be very slow. In this means, the long term experiments are important and were performed in this project.

The (ir)reversibility of coagulation process is important issue. If the coagulation process is fully reversible, the change of geochemical condition will lead to aggregation or disaggregation of clay colloids once again (e.g. in Scandinavian Deep Geologic Repository –

DGR - concept the cycle of glacial and interglacial periods). If the hysteresis of coagulation process takes a place, the aggregation or disaggregation of clay colloids will not undergo in the same dimensions. This phenomenon was studied within this project.

The presence of organic substances in DGR is expected to be associated with host rock itself, microbial and anthropogenic activities and materials used in the construction. Because the interaction between the clay colloids and organic molecules greatly influences its stability part of work was dedicated to this phenomenon.

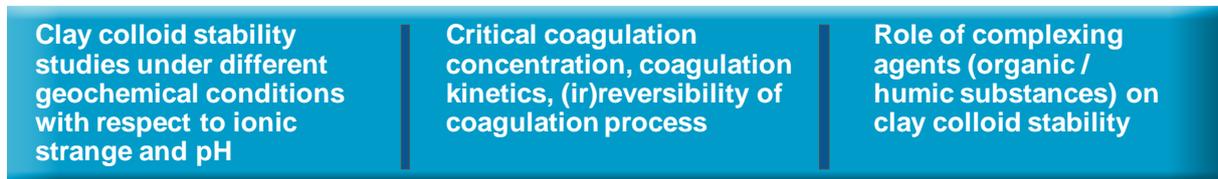


Figure 2: Selected issues in WP4 with respect to long term safety of DGR.

This final report summarizes the main outcomes of WP4 and achieved highlights with respect to given issues in WP1.

## Phase (state) diagram of montmorillonite (ClayTech)

The clay minerals of smectite group (e.g. montmorillonite) are main constituents of bentonite. These 2:1 type clay minerals impart to bentonite specific properties such as for example swelling or high cation exchange capacity. The bentonite barrier will be in interaction with groundwater of specific chemical composition, which will be resulting in different phases (states) in such system. A schematic phase or state diagram for Na-montmorillonite in contact with NaCl(aq) is shown in Figure 3. It contains the phases: sol, attractive gel and repulsive paste (repulsive gel). In principle the same diagram could be used for a mixed Ca/Na system as long as the behaviour is not dominated by the ion-ion correlations, i.e. the amount of Na<sup>+</sup> in the interlayer is > ~20%. For the mixed system, the ionic strength has to be set by a mix of CaCl<sub>2</sub> and NaCl to avoid exchange. This more complicated type of phase diagram has been discussed previously in terms of the sol-formation zone (Birgersson et al., 2011, 2009).

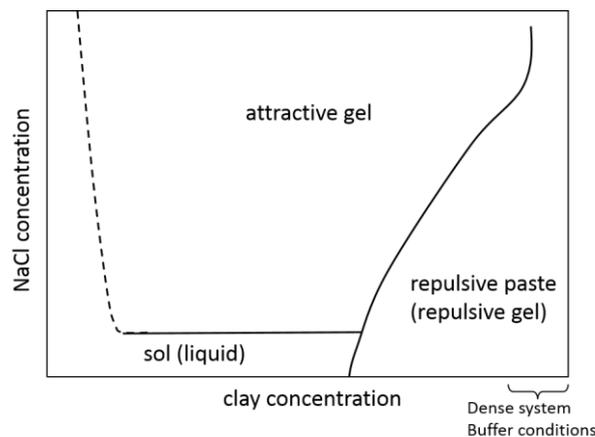


Figure 3: Schematic phase (state) diagram for Na-montmorillonite.

**Repulsive paste** - at high clay concentration the repulsion forces (osmotic double layer forces and hydration) dominate the system and the yield stress that the system displays is a

consequence of jamming. This phase also displays significant osmotic pressure, particularly in the denser region that is representing the conditions for the buffer. In this dense region salinity has little qualitative effect on the system. Even at high NaCl concentrations ( $> 3\text{M}$ ) the osmotic pressure never vanishes (Karlund et al., 2006). At lower clay concentration the repulsive system may show liquid crystalline behaviour and an isotropic to nematic transition has been observed (Michot et al., 2004). Below the critical coagulation concentration (CCC) the repulsive paste would eventually turn into a sol if it has free access to solvent and the volume is not restricted.

**Montmorillonite sol** - the sol phase is a suspension of montmorillonite particles (individual layers or aggregates) that are only weakly interacting. We have previously shown that aggregates are formed in the sol phase even when the clay is dispersed in deionized water (Birgersson et al., 2009) and recent theoretical work suggests the apt term disconnected house-of-card for such structures (Angelini et al., 2014). These aggregates have limited size and do not form a network that span the available space, hence no yield strength. Edge-to-face interaction is most probably the cause for aggregate formation. Over long time periods, aggregates may accumulate at the bottom of a vessel as a sediment. The sediment has no observable yield strength.

Making sols stable has been a major effort in colloid science and technology, and one can readily appreciate the importance when it comes to products such as paints or household cleaners. The sol is stable if the repulsion extends beyond the distance where the attractive potential minimum is about  $k_B T$  or less. If we for the sake of argument assume the naive idea that face-to-face van der Waals interaction is the cause for coagulation in Na-montmorillonite, we can estimate how close two clay layers need to be in order to be bound. In the Hamaker treatment of the van der Waals interaction energy  $U_{\text{vdw}}$  is given by:

$$\frac{U_{\text{vdw}}}{\text{area}} = -\frac{A_H}{12\pi} \left( \frac{1}{h^2} + \frac{1}{(h+2\delta)^2} - \frac{2}{(h+\delta)^2} \right), \quad (1)$$

where  $\delta$  is the thickness of a clay layer ( $\sim 1\text{ nm}$ ) and  $A_H$  is the effective Hamaker constant that incorporates the material properties of the colloidal particles and the intervening medium. The separation between the clay layers is denoted by  $h$ . A realistic area of a montmorillonite layer is  $10^5\text{ nm}^2$ , e.g., (Ploehn and Liu, 2006). Using this value and  $A_H = 5 k_B T$ , Eq. (1) then predicts  $|U_{\text{vdw}}| < 1 k_B T$  when  $h > 16\text{ nm}$ . Thus if the range of the repulsive force is longer than 16 nm, the van der Waals interaction will be insufficient to cause coagulation. A separation of 16 nm may seem large, especially compared to the buffer condition where the interlayers have either two or three layers of water molecules corresponding to separations of approximately 6 or 9 Å, respectively. However, compared to the lateral dimensions of the clay layers, 16 nm is still a small separation as shown by the scale drawing in Figure 4. The volume fraction of clay in this case is  $\phi_c \approx 1/17$  which corresponds to a mass concentration of 160 g/l. At the experimentally determined critical coagulation concentration for Wyoming Na-montmorillonite,  $\sim 20\text{ mM NaCl}$ , the calculated osmotic pressure at  $\phi_c \approx 1/17$  is about 1.4 kPa. Thus one can conclude that face-to-face van der Waals interaction contributes marginally to destabilizing Na-montmorillonite sols.



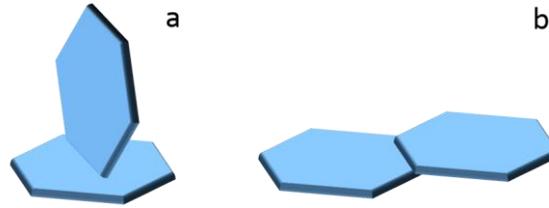
**Figure 4: Side view of two montmorillonite layers at a separation where the van der Waals attraction is of the order of  $k_B T$ .**

**Attractive montmorillonite gels** - attractive gels are formed above a critical concentration of electrolyte. In the present work the influence of NaCl on gelation has been investigated in particular. Above the CCC a gel phase is formed. This attractive gel can be produced by either letting montmorillonite swell in a solution with NaCl concentration above the CCC or by adding NaCl to a montmorillonite sol such that the final NaCl concentration is above the CCC. In the former case the gel would swell until it meets the boundary separating the repulsive paste from the attractive gel (Figure 3). In the latter case we have found that a very low density gel can be formed where the average clay concentration may be more than an order magnitude smaller than the clay concentration at which the clay particles can start to rotate freely. A credible conceptual view of this attractive gel is a loose percolated network (Tanaka et al., 2004) of clay layers interacting through edge-to-face attraction. An example of such a gel is shown in Figure 5. The following can be inferred from this figure: (i) attraction forces must be the cause for keeping the gel together and give it yield strength. Although repulsive interactions can give arrested states (repulsive paste), such a structure would not be stable and occupy only a part of the total available electrolyte volume. The gel in Figure 5 has remained unchanged for more than five years, showing that it withstands gravity, thermal fluctuations and potential osmotic forces. (ii) face-to-face van der Waals interactions can be totally ruled out at  $\phi_c \approx 7 \cdot 10^{-4}$ ; (iii) overlapping coin configurations must to a large extent contribute to the structure, because a gel with only T-shaped configurations would have a much higher  $\phi_c$  (Figure 6).

At sufficiently low clay concentration the clay layer density is below the percolation threshold, i.e. a space-filling network cannot be formed even if the ionic strength is above the CCC. This percolation threshold is indicated with a dashed line in Figure 3. The precise location of this border has not been explored in this study. The attractive gel would collapse under gravity before one actually reaches the percolation limit.



**Figure 5: Snapshot of Ku-Na gel taken ca three years after formation in a mixed NaCl/NaOH solution of ionic strength 15 mM and pH ~11. Initially the vial was standing upright and filled with a montmorillonite sol of 2g clay/l that was sedimenting and slowly gelling and consolidating. After the gel was formed, the vial was placed horizontally and the gel eventually unfastened from the glass and flipped forward. Most of the clay particles actually sedimented before gelation took place which is why there are darker rings of material at what is now the top of the gel. Based on turbidity we estimate the clay concentration in the gel to be less than 2 g/l, equivalent to a volume fraction of 0.07%.**



**Figure 6: Proposed arrangements for edge-to-face interaction: a) T-shaped configuration, leading to house-of-cards structure. b) Overlapping coins configuration that gives band-like structures.**

As mentioned above, edge-to-face interactions are necessary for gelation of montmorillonite. Measurement on dilute montmorillonite sols, suggests a rather strong pH dependence on the stability ratio (Tombácz and Szekeres, 2004) and it seems reasonable that an increase in pH would promote deprotonation of titratable edge groups. However, conclusions often drawn from such experiments, that the edge charge can only be positive below pH 6.5 and at slightly alkaline conditions the edge is negative cannot be generally valid as they would be at odds with the observed effect of pyrophosphate on gelation and rheology.

Pyrophosphate anions have large influence on the formation of montmorillonite gels as the anions bind to the positive edge and thereby block the edge-to-face attraction. The addition of 0.25% tetra sodium pyrophosphate to 0.5% w/w Wy-Na suspensions increased the CCC for NaCl by almost an order of magnitude (Birgersson et al., 2009). Similarly addition of pyrophosphate to an existing gel was found to lead to an almost instantaneous disintegration of the gel. These observations are completely in line with recent rheological measurements on bentonite slurries (7% w/w) where it was found that the addition of polyphosphates totally removed the yield strength over the pH range 5-10 and drastically reduced the yield strength below pH 4 (Goh et al., 2011). Without adding polyphosphate, the yield strength was significant ~30 Pa even at pH 10, which led the authors to draw the inevitable conclusion that: “The nature of the clay particle edge charge must still be positive at this high pH level”. Birgersson et al. (2009) tested the influence of pH on the formation of Wy-Na gel and found that a gel was formed at 25 mM NaCl (close to the CCC) also at the highest tested pH value of 9.1. Similarly, in erosion tests using artificial fractures, erosion have not been observed for Wy-Na provided that the NaCl concentration is above 20-25 mM even at pH up to 10.

## **Experimental determination of the phase/state diagram for three montmorillonites**

Montmorillonite extracted from three types of bentonite have been used during these investigations: Wyoming-type (Wy) obtained from MX-80 bentonite (American Colloid Co.), Kutch-type (Ku) obtained from the Indian bentonite Asha 505 (Ashapura Minechem Co.) and Milos-type (Mi) obtained from the Greek bentonite IBECO Deponit CA-N (Silver & Baryte Mining Company S.A.). The montmorillonites were purified and ion-exchanged with NaCl to the homoionic form according to the procedure described in Karnland et al. (2006). The purified montmorillonites are referred to as Wy-Na, Ku-Na and Mi-Na, where Na is the counterion. The chemical formula for an ideal sodium montmorillonite, interlayer water excluded, can be written as  $[(\text{Si}_{8-\alpha}\text{Al}_{\alpha})(\text{Al}_{4-\beta}\text{Mg}_{\beta})\text{O}_{20}(\text{OH})_4]^{(\alpha+\beta)-}\text{Na}^{+\alpha+\beta}$ , where by definition the tetrahedral charge is lower than the octahedral charge ( $\alpha < \beta$ ) and the sum of tetrahedral and octahedral charges fulfil  $0.4 < \alpha + \beta < 1.2$ .

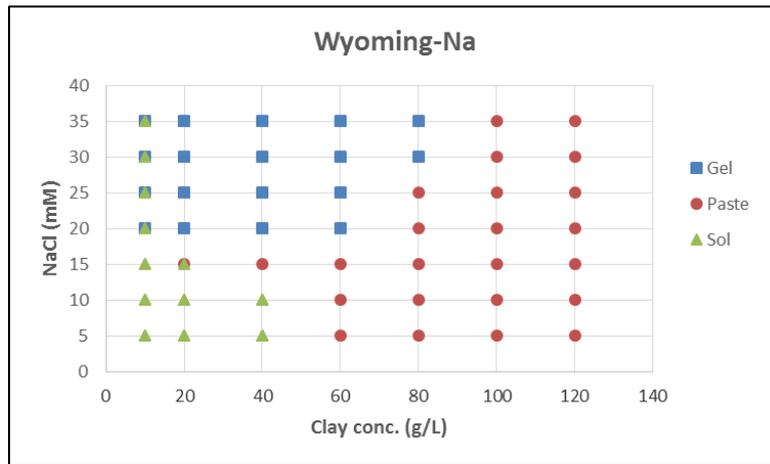
Clay samples were prepared with specific clay and salt concentrations at fixed volumes, according to the following protocol. Clay was dispersed in deionised water. Aqueous NaCl

solution was added so that the overall sample volume as well as clay and salt concentration were the intended ones. This salt solution was also called the internal salt solution, and the salt concentration of the internal solution was adjusted so the system would be in or near ion equilibrium with what we will term the external NaCl concentration. The determination of the internal concentration was done by solving the Poisson-Boltzmann equation under the assumption/approximation that the clay particles were evenly distributed within the suspension volume initially occupied by clay (Hedström and Karnland, 2012). The volume of the clay sample was marked before external NaCl solution was added to fill the vial to the top. If the clay sample appeared to behave as a solid, the sample vial was laid down on its side. If not, the sample vial was left standing up. The clay sample was regularly checked for signs of different colloidal states by visual observation. The preparation of a representative sample (40 g Wy-Na/l, 5 mM NaCl) is described as following: The total clay sample volume was 2 ml. Therefore, 80 mg Wy-Na was dispersed in 1 ml of deionised water. The Poisson-Boltzmann equation gives the internal NaCl concentration as 3.8 mM in order to be in equilibrium with 5 mM external solution. Therefore, 1 ml of 7.6 mM NaCl solution was then added and the sample was mixed. The 2 ml clay sample volume was marked before the external 5 mM NaCl solution was added to the sample which was then sealed and laid down on its side. Representative examples of how the three major different states were identified are shown in Figure 7.

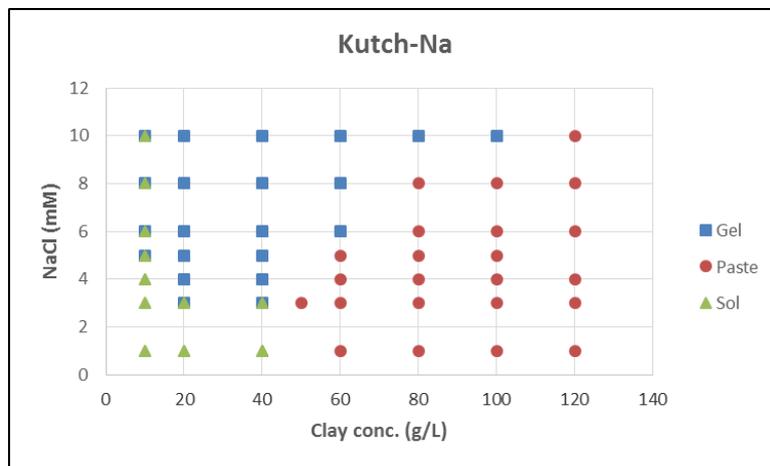


**Figure 7: a) Gel. No expansion past the initial sample volume. b) Repulsive paste. Expansion of the initial sample volume. Final state is a gel, presumably reflecting the gel/paste border. c) Example of sol. Exhibits flow. In this sample there is a well-defined boundary between the sol and the aqueous phase. A sol could also behave more like a gas with clay particles diffusing into the whole volume.**

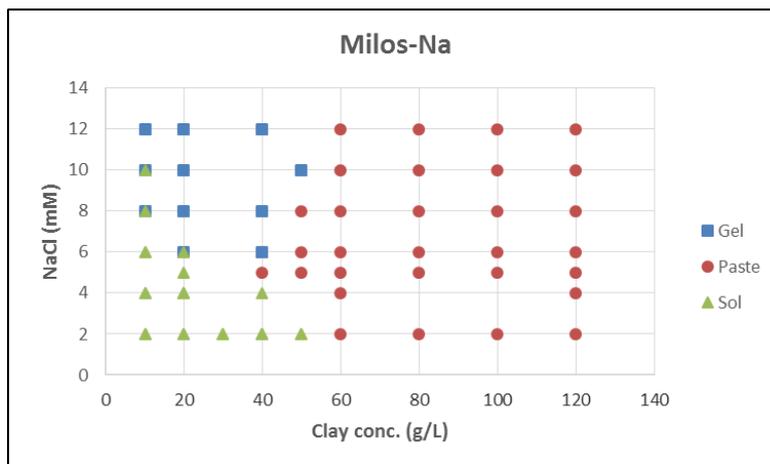
The method used for classifying the states gives unambiguous results for gels and pastes above the CCC. However the paste/sol border is less well mapped because of the addition of solution on top of the initial clay dispersion. Below the CCC a paste tend absorb more liquid and thereby eventually become liquid and flow when the vial is placed horizontally. In the phase diagrams below (Figure 8 to Figure 10) such behaviour was observed for the samples with clay concentration 40 g/l. Thus they are marked as sols in the diagrams but are actually pastes. Above the CCC at clay concentration 10 g/l, samples are denoted as both sol and gel. These states are actually gels but are rather weak so there was a certain degree of sedimentation before gelling took place. However, below the CCC gelling does not occur, only sedimentation. Note that the CCC is different for the three different clays. Wy-Na at 15 mM NaCl are either sols or pastes, while at 20 mM a gel can be formed. Thus CCC between 15 and 20 mM NaCl. In the case of Ku-Na the CCC is located between 3 to 4 mM, whereas for Mi-Na CCC is found at 6 mM.



**Figure 8: State diagram of Wy-Na montmorillonite.**



**Figure 9: State diagram of Ku-Na montmorillonite**



**Figure 10: State diagram of Mi-Na montmorillonite.**

When a gel is formed it is straightforward to judge what is external electrolyte and what is gel since the gel create its own membrane. If no swelling is detected one knows that the clay concentration and external electrolyte concentration are such that the gel state is the

equilibrium state. When swelling occurs the initial state exerts a swelling pressure and is thus dominated by repulsions, which we term a paste. The method is less accurate when determining the actual equilibrium states below the CCC. Again from the bentonite barrier application point of view the CCC or the gel-sol or gel-paste line still represent the NaCl concentration where eventual loss of bentonite may occur, either through further swelling into fractures or transported away by flow.

These investigations suggest that, provided the ionic strength of the ground water is above the CCC, the highly compacted clay in engineered barriers will act as a swelling repulsive paste and expand. Once the lowest clay concentration at the swelling front is below the clay concentration required for paste formation, the clay will form a gel. The lowest limit appears to be about 60 g/l, although it can be higher depending on the type of montmorillonite as well as the salinity in the surrounding system.

## Rheology of attractive montmorillonite gels (ClayTech)

To give quantitative support to the notion that the formation of an attractive gel would prevent erosion, the yield strength of dilute Kutch montmorillonite (Ku-mmt) gels at various NaCl concentrations was determined by means of rotating vane rheometry using a Brookfield DV II + Pro LV viscometer and the V-73 vane spindle. The vane was lowered into the clay sample and the measurement was started immediately. The yield-stress measurement was conducted at a low constant rotational rate of 0.05 rpm for 500-800 s. The yield stress is taken as the peak value in the stress-time curve (equivalent to stress-strain curve).

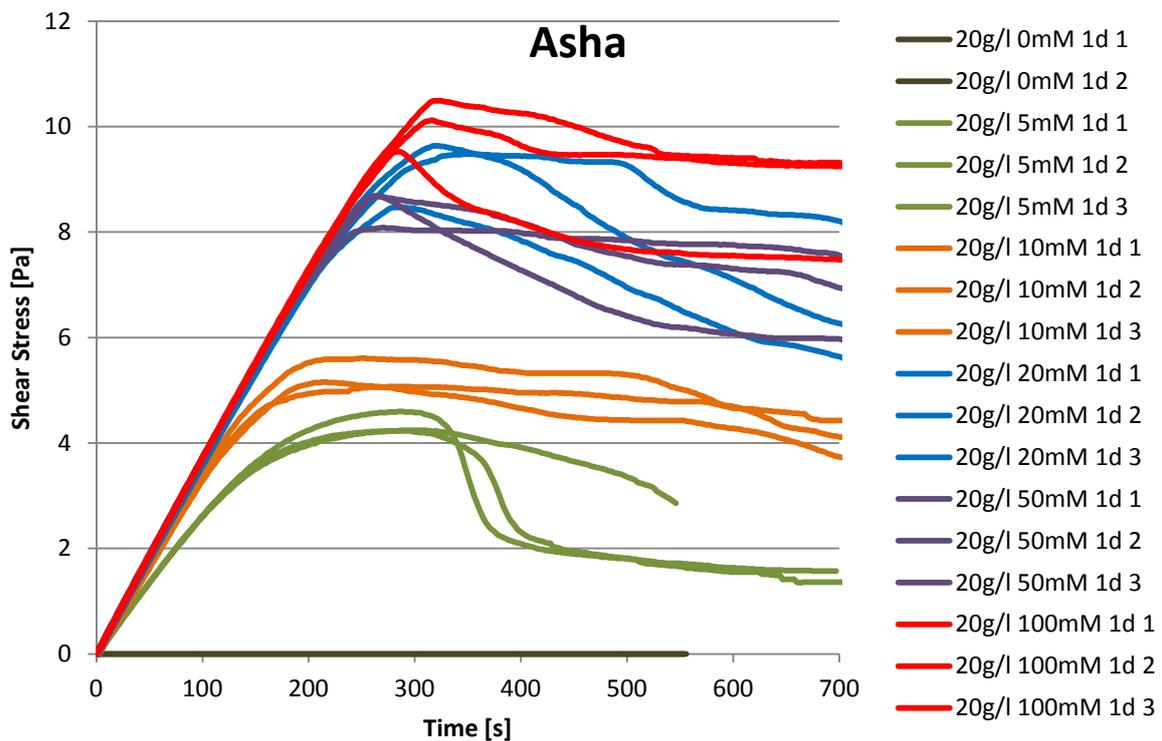
**Material** - raw (as received) Asha505 bentonite was dispersed in deionized (DI) water (10 g/l) and sonicated for 15 minutes. Then the suspensions were left on magnetic stirrer overnight. The  $< 2 \mu\text{m}$  fraction, which essentially consists of montmorillonite, was extracted from the bentonite suspension using centrifugation. The suspension containing the  $< 2 \mu\text{m}$  fraction was placed in  $60 \text{ }^\circ\text{C}$  oven until the water had evaporated (approximately 3 days). The oven-dried montmorillonite was subsequently milled to a fine powder. Note that the montmorillonite is not homo-ionized. A previous determination of exchangeable ions showed that the montmorillonite fraction of Asha 505 contains  $\text{Mg}^{2+}$  (28 %),  $\text{Ca}^{2+}$  (31 %),  $\text{Na}^+$  (40 %), and  $\text{K}^+$  (1 %) (Karlund et al., 2006).

**Sample preparation** - stock dispersions (20 g/l and 40 g/l) of Ku-mmt were prepared by mixing the montmorillonite powder with DI water using magnetic stirrer. After  $\sim 20$  h the dispersions appeared homogeneous and smooth. After  $\sim 24$  h the dispersions were added to NaCl solutions. Each sample cup was filled with 15 ml of NaCl(aq) (double strength) and 15 ml of Ku-mmt stock dispersion was added. The sample was capped and vigorously shaken 50 (5 and 10 mM final ionic strength) or 100 times (50 and 100 mM final ionic strength) and left to rest (1 day or 1 week) before the rheology tests. After examining the yield-stress results from the first series of experiment, we decided to also perform tests on Ku-mmt in 20 mM NaCl(aq). Those samples were neither prepared from the same stock dispersion, nor by the same person.

Figure 11 shows the shear stress vs. time for Ku-mmt at 20g/l and different NaCl concentrations. Without added NaCl the shear stress is zero which indicates a sol. At 5 mM NaCl and above the shear stress is significant. A summary of the average maximum yield stress is presented in Table 1. The yield stress increases with clay concentration and aging.

**Table 1: Average yield stress from the rheological measurements on Ku-mmt gels. 24 h and 1 week in the table refer to the rest time between sample preparation and measurement.**

C <sub>mmt</sub> [NaCl]		Average maximum yield stress (Pa)			
		10 g/l, 24 h	10 g/l, 1 week	20 g/l, 24 h	20 g/l, 1 week
5 mM		0.4	1.1	4.4	7.7
10 mM		1.5	2.8	5.3	8.0
20 mM		-	-	9.2	8.9
50 mM		2.5	3.5	8.5	-
100 mM		2.6	3.9	10.0	-



**Figure 11: Shear stress vs. time for Ku-mmt at a concentration of 20 g/l and different NaCl concentrations 24 hours after preparation. Note that without extra NaCl, denoted 0 mM in the legend, the suspension has no yield stress at all, and the two curves coincide with the x-axis.**

The present tests show strong sensitivity to the salinity of the external water. For Ku-mmt a NaCl concentration of ~5 mM is needed to form a gel. However, even at such low concentration the present tests show that the yield stress is significant. In fact, all tested gels have yield stresses several orders of magnitude higher than the anticipated drag force of the flowing water in a repository (Eriksson and Schatz, 2015). The yield stress also shows strong dependence on clay concentration. This dependence is even stronger than that on salinity. The highest clay concentration in this study is 20 g/l, but at a repository one may expect higher clay concentrations at the repulsive-attractive gel border adjacent to the ground water, cf. the Ku-Na state diagram in Figure 9. In the present study we also reconfirm the effect of aging. One week of resting produce significantly stronger gels than those tested after 24 hours. At installation of the buffer bentonite in a future repository, the ground water conditions are such that an attractive gel will be formed at the swelling front and strongly limit penetration of

bentonite into water-bearing fractures. These conditions will prevail at least until the next glaciation. Thus the attractive gel, most probably will attain its maximum strength.

## **Bentonites characterization (CIEMAT)**

For further stability studies and characterization five different bentonites were selected: FEBEX bentonite from Spain (Huertas et al., 2000); IBECO bentonite from Mylos island in Greece (Koch, 2008); MX-80 bentonite, Wyoming, USA (Müller-Vonmoss and Kahr, 1983); Bentonit 75 (denoted as B75) partly Na-activated bentonite, Rokle, Czech Republic (Konta, 1986) and a Russian bentonite from the Khakassia deposit (Sabodina et al., 2006).

One of the possible causes of the difference in the stability / erosion behaviour could be related to the different mineralogy of the different bentonites. A complete geochemical and mineralogical characterization was carried out by different techniques (e.g. XRD, FRX, FTIR, TG-DSC) to evaluate major and minor minerals, clays content, cation exchange capacity, major cations, water content, porewater chemistry, charge distribution and cell formula of the five bentonites. Full details on the characterization can be found in Fernandez (2013).

## **Stability studies (CIEMAT, ÚJV, KIT-INE)**

### **Role of anorganic compounds**

Apart from the smectite (as main component of the bentonite) and its properties, other elements may affect the overall behaviour of the clay barrier, namely the presence of other clay minerals or oxides. Thus, stability studies were carried out not only with different raw bentonites but also with other clay minerals and smectite/mineral admixtures. In summary, different types of studies were carried out at CIEMAT:

1. Comparative analysis of the stability of different bentonites, previously exchanged in Na, as a function of pH and ionic strength;
2. Stability of different clay minerals (illite, saponite, kaolinite), previously exchanged in Na, as a function of pH and ionic strength;
3. Effect of the additions of various minerals (clay minerals or oxides) on the stability of smectite (FEBEX);
4. Comparative analysis of colloids extracted from different raw bentonites and analyses of their aggregation upon Na or Ca additions.

The stability of colloid suspensions obtained from the different Na-exchanged clays was studied as a function of the pH and ionic strength in  $\text{NaClO}_4$ . Electrophoretic measurements, allowing determining the surface potential of the clay particles (Zetapotential) and Photon Correlation Spectrometry (PCS) were used to measure the mean size of the particles under different conditions. In the case of the raw clays, which were initially dispersed in deionised water, the initial concentration and size of the particles was measured and their stability was studied upon small progressive additions of  $\text{Na}^+$  or  $\text{Ca}^{2+}$ . In this way, the concentration of monovalent or divalent cation needed to start coagulation process in the clays could be determined.

Zeta potentials were determined with a Zetamaster Malvern system equipped with a Spectra-Physics 2mW He-Ne laser ( $\lambda = 633 \text{ nm}$ ). The size of the particles was measured with a Malvern NanoS apparatus with He-Ne laser and at a measurement angle of  $173^\circ$ .

## **Stability behaviour of different Na-bentonites, clay minerals and mineral admixtures**

As already described in Deliverable D4.8 (Alonso et al., 2015), the comparison between the zeta-potentials of the different exchanged bentonites, as a function of the pH, at ionic strength of  $5 \cdot 10^{-4} \text{ M}$  ( $\text{NaClO}_4$ ) indicated that the zeta-potential of all the clay colloids is negative and almost independent of the pH; the maximum variations observed considering all the clays were within 15 mV (from -48 to -35 mV). Furthermore, PCS measurements performed as a function of the pH and the ionic strength in the Na-exchanged clays showed that most clay colloids present evident aggregation at 0.01 M in  $\text{NaClO}_4$ , which was accentuated at acid pH, due to edge-face interactions.

In all the cases, the colloid size remained almost unvaried up to  $I = 1 \cdot 10^{-3} \text{ M}$  even if a slightly increase for pH lower than 4 were observed. At  $I = 0.1 \text{ M}$ , colloids from all the clays were completely destabilized with size outside the colloidal range. In general, it was observed that zeta-potential and the aggregation behaviour of the Na-exchanged bentonites, was not very different from one case to another.

The zeta-potential in a 2:1 clay mostly depends on the permanent layer charge, therefore this is mainly determined by the major mineral (smectite) present in the bentonite and it is insensitive to the presence of other minerals in low concentrations. However, in spite of the similar stability behaviour observed first erosion experiments clearly showed certain differences in the erosion of the different clays (Deliverable D2.7, Missana et al., 2015).

The main clay component of the bentonites is the mineral smectite and from previous tests it was deduced that the degree of erosion could be related to the quantity of smectite in the system. For example, the generation of colloids in the smectite/illite system was fairly proportional to the smectite content. The natural illite du Puy, France (Gabis, 1958) was selected to carry out erosion and stability experiments in admixtures with the FEBEX clay. However the addition of kaolinite, (Kaolinite KGa-1-b, obtained from the Clay Mineral Society) inhibited the generation of the colloids from the bentonite.

The analysis of the stability of smectite/illite, smectite/kaolinite and smectite/ $\text{Al}_2\text{O}_3$  colloids in admixtures was also previously described in Deliverable D4.8 (Alonso et al., 2015). It was observed that illite does not affect bentonite stability, but both the addition of kaolinite or  $\text{Al}_2\text{O}_3$  nanoparticles to bentonite promoted colloid aggregation under certain conditions. The observed bentonite colloid destabilization might be the cause of the inhibition of bentonite erosion in the compacted system and these facts remarked the importance of stability studies for the understanding of the barrier erosion.

## **Stability behaviour of different raw bentonites**

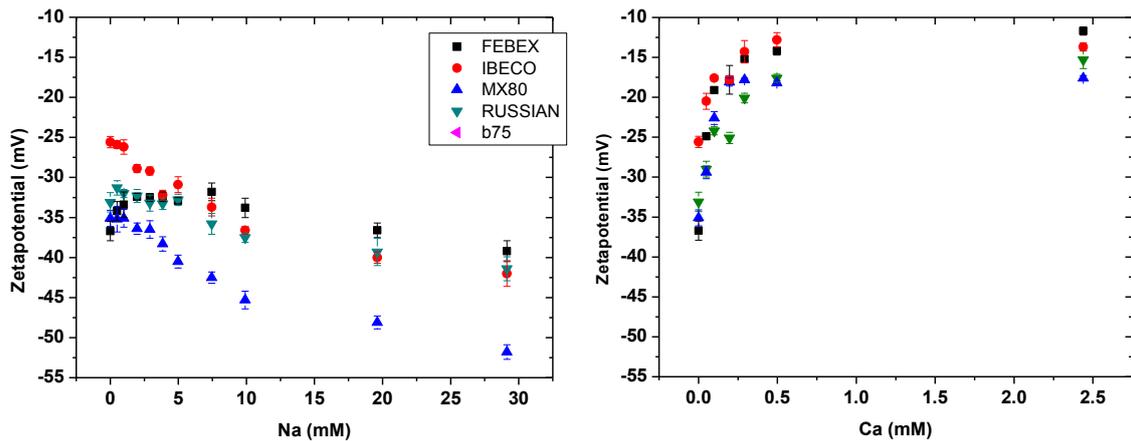
The intrinsic physico-chemical properties of the different bentonites are also expected to play an important role on the overall stability and erodibility of the clay. For this reason the behaviour of the raw bentonites was also comparatively analyzed to understand with more detail the differences between the different materials.

Colloids were extracted from the different raw clays by dispersing them (1 g/L) in deionized water and collecting the supernatant after centrifuging at approximately 600·g during 10 minutes. The water in equilibrium with the solid phase was analyzed to account for the presence of ions leached directly from the clays, to be accounted for in further detailed analyses. The quantity of colloids present in each case in the supernatant was measured by gravimetry (Table 2), and this provided the first indication of the clay capability of dispersing colloidal particles under favourable chemical conditions (*i.e.* deionized water, DW). For the selected bentonites, which are Na or Ca-Mg bentonites (but with at least 20 % of Na in the exchange complex), the concentration of colloids remained in suspension after centrifuging, correlated quite well with the quantity of Na in the exchange complex: the higher the Na in the clay, the higher the concentration of particles in solution. The initial size of these colloids was measured by Photon Correlation Spectrometry. For the selected bentonites, as observed for the initial colloid concentration, the colloid size was also very similar, ranging between 300 and 400 nm. The difference in the measured size also correlated quite well with the Na content in the exchange complex: the higher the Na in the clay, the smaller the particle size. These results confirms again what observed in previous tests, *i.e.* that the stability/generation behaviour of Ca-Mg clays is similar to that of Na-clays provided that enough Na is present in the exchange complex (>20 %).

Other parameters are being investigating with other smectites, in addition to those presented in this report, trying to cover a wide range of possible different properties (tri-octahedral vs. di-octahedral clays, different exchange complex, different charge density, different charge location). The complete results will be presented in a paper which is in preparation (Missana et al., 2016). It will be just mentioned here that, in general, those clays having the charge located in the tetrahedral layer forms larger colloids: these particles sediment easier being less stable than others (Missana et al., 2016) even in DW. This is related to the generation behaviour of colloids from the compacted clay barrier, which will be discussed in detail elsewhere.

**Table 2: Summary of main data obtained from the stability experiments with raw clays. n.d. = not determined**

<b>BENTONITE</b>	<b>Concentration of particles by gravimetry (mg/L)</b>	<b>Initial Size in DA</b>	<b>Onset coagulation (Na, mM)</b>	<b>Onset coagulation (Ca, mM)</b>
<b>FEBEX</b>	166±20	351	7-10	0.2
<b>MX-80</b>	178±10	336	5-7	0.2
<b>IBECO</b>	157±10	395	2-3	0.1
<b>B75</b>	n.d.	n.d.	n.d.	n.d.
<b>RUSSIAN</b>	260±10	304	5-7	0.2



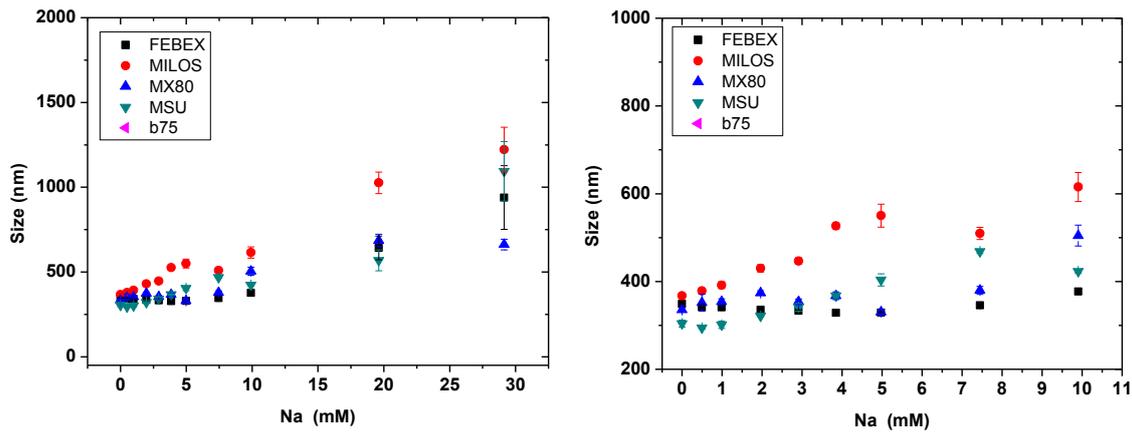
**Figure 12: Zeta-potential measured at different concentrations of added Na (left) and Ca (right) for the different clays.**

After the characterization of the colloids directly dispersed from the raw clays, stability tests were carried out performing small progressive additions of  $\text{Na}^+$  or  $\text{Ca}^{2+}$  and measuring the variation of mean colloid size and of the electrophoretic potential. In this way, also the concentration of monovalent or divalent cation needed to start coagulation process in the different clays could be also determined.

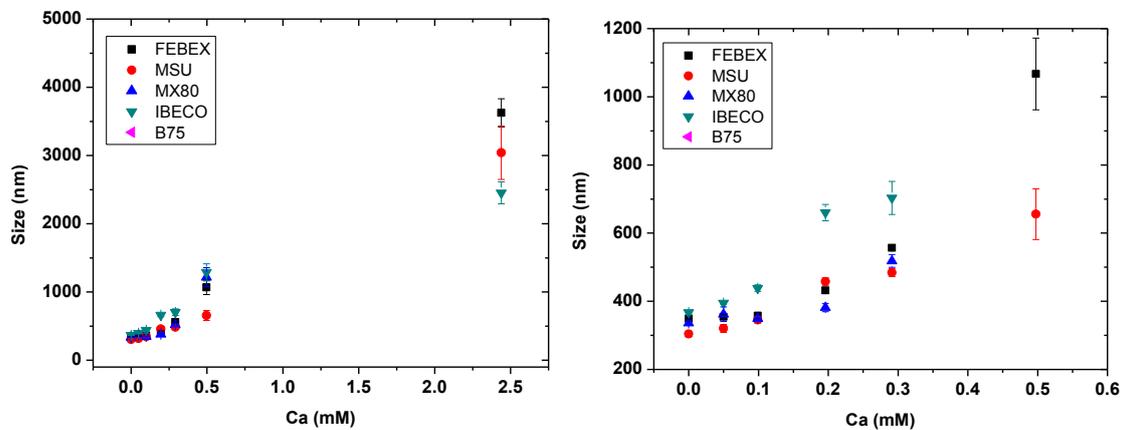
Figure 12 shows the zeta-potential measured at different concentrations of added Na (left) and Ca (right) for the different clays. In general, the progressive additions of Na produced a slow decrease in the negative value of the zeta-potential up to a plateau value around -40 mV for most of the clays. The behaviour observed, after the very first Na additions, is not exactly the same for all the clays and might be related to the leaching of Ca from the clay and Na-Ca exchange processes. In fact, almost all the clays suspended in deionised water released Na, Ca or Mg ions for dissolution of soluble salt impurities or of the clay itself. The clay that reaches more negative values at the plateau (around -50 mV) is the MX-80.

The addition of Ca, on the other hand, produces a pronounced and rapid decrease in the negative zeta-potential value with respect to the initial untreated sample. This variation is similar in all the cases, but it is less sharp for the clays having predominantly sodium in the exchange complex. The value at the plateau for all the samples after Ca addition is around -15 mV.

Figure 13 shows the size of the clay colloids after the additions of Na (complete measurements in the left part and magnification of the figure for low Na concentrations in the right part). The increase of Na concentration, clearly produces clay colloid aggregation in all the cases, even if most of the clays present particles in the colloidal size range ( $< 1 \mu\text{m}$ ) even after the addition of 20-30 mM of Na. However, the onset of aggregation occurs for concentration of Na between 2 and 7 mM, similarly for all the clays (in accordance with D4.7, Hedström et al., 2014).



**Figure 13: Size of the clay colloids after the additions of Na (complete measurements in the left part and amplification at low Na concentrations in the right).**



**Figure 14: Size of the clay colloids after the additions of Ca (complete measurements in the left part and amplification at low Ca concentrations in the right).**

Figure 14 shows the size of the clay colloids after the additions of different Ca concentration (complete measurements in the left part and magnification of the figure for low Ca concentrations in the right part). Also in this case, the aggregation behaviour is similar for all the selected clays and the onset of coagulation is around 0.1 - 0.2 mM (more than one order of magnitude lower of Ca is needed for aggregating the particles with respect to Na, as expected). For Ca concentration larger than 0.5 mM most of the clay particles aggregates to give size larger than 1  $\mu\text{m}$ .

In all the studies carried out at CIEMAT it has been observed that the parameters that guarantee the stability of clay colloids are necessary conditions (even not sufficient) for the possible erosion of the clay barrier. Thus, colloid stability studies are necessary and very important in this context.

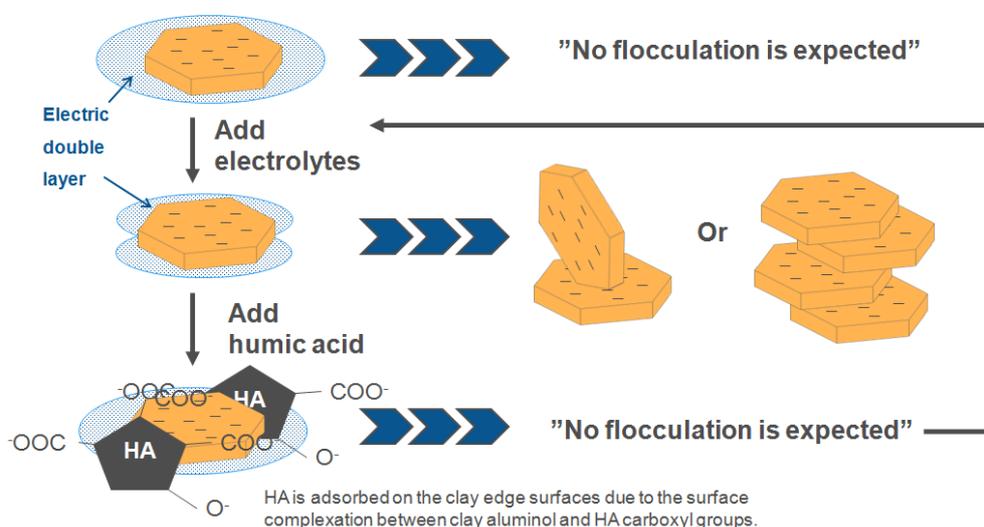
The presence of Na in the exchange complex favours clay dispersion and makes the colloidal particles smaller. However, it has been shown that clay colloid aggregation is triggered by the presence of Na (10 mM) or Ca (0.1-0.2 mM) in solution indicating that they will not be stable with higher concentration of these ions.

Sodium and potassium, and magnesium and calcium act in similar way during the coagulation process and in real systems (e.g. natural groundwater) their effect can be simplified to the effect of  $M^{1+}$  (Na+K) or  $M^{2+}$  (Ca+Mg) cations, where  $M^{2+}$  are more effective in coagulation.

The interaction of smectite with mineral like kaolinite or  $Al_2O_3$  produces the aggregation of particles that, alone under the same chemical conditions would be stable; this means that the presence of certain minerals not only inhibits the clay colloid generation “by dilution” of the smectite, but also may affect the properties of the smectite itself making the system unstable.

## Role of organic compounds

The presence of organic substances in DGR is expected to be associated with host rock itself, microbial and anthropogenic activities and materials used in the construction. The interaction between the clay colloids and organic molecules greatly influences its stability. Studies were focused on humic and fulvic acids, which are natural organic substances often occurring in surface waters and near-surface groundwaters. One potential way, how the humic acids act as stabilizers and protect the clay particles against the coagulation, is shown in Figure 15.



**Figure 15: The schematic picture of humic acid stabilization effect on clay particles.**

Two kinds of bentonite Czech Bentonite 75 (denoted as B75) and Wyoming type MX-80 were used for investigation. Bentonite B75 was purified and converted to  $Na^+$  form before the experiments. The effect of clay colloids stabilization by humic acid in  $NaCl$  and  $CaCl_2$  electrolytes was investigated. The MX-80 bentonite colloid stability was examined systematically under different chemical conditions, starting from a delaminated bentonite clay suspension (for preparation of the clay colloidal stock suspensions see D4.5, Bouby et al., 2014).

## Fast coagulation experiments

These studies were performed using PCS measurements according to the experimental protocol described in Behrens et al. (2000), Czigány et al. (2005), Holthoff et al. (1996), Kretschmar et al. (1998).

The clay colloid concentration was fixed to 10 mg/L by prior and further dilution in the same aqueous media (1 to 6) with or without additional fulvic acids (FA) at 2.5 mg/L (1.5 mg/L NPOC). The composition of the aqueous media is the following: 1) MQ at pH 5.7, 2)  $NaCl$

1.3  $10^{-3}$  M at pH ~5.7, 3)  $\text{CaCl}_2$  0.433  $10^{-3}$  M at pH ~5.7; 4)  $\text{NaHCO}_3$   $10^{-3}$  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 (1.3  $10^{-3}$  M IS) with  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , trace of  $\text{Si}$ , with or without  $\text{HCO}_3^-$  giving thus 2 different pHs.

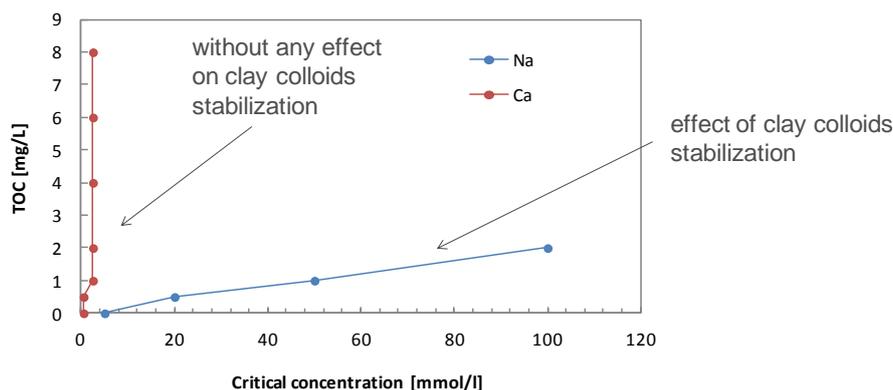
The ionic strengths (IS) examined were 0.1 M, 1 M and 3 M set by using the electrolytes  $\text{NaCl}$ ,  $\text{CaCl}_2$  or  $\text{MgCl}_2$ . The pHs are indicated Table 3. They are very close to those of the aqueous media used for the preparation of the clay colloid stock suspensions, see D4.6 (Bouby et al., 2014). The initial intensity-weighted hydrodynamic mean diameter is first measured during 45 s and the corresponding values are reported Table 3. Note that in presence of  $\text{CaCl}_2$  (aqueous media number 3), the clay colloids present an initial mean hydrodynamic diameter significantly larger than in the other aqueous media. The calcium ion is thought responsible, acting as a coagulant, even if only present at low concentration (0.433  $10^{-3}$  M). This was already observed in Bouby et al. (2011). The presence of FA might have slowed down this process (see Table 1). This has to be further investigated. The evolution of the hydrodynamic diameter of the clay colloids is monitored after the addition of concentrated electrolyte aliquots ( $\text{NaCl}$ ,  $\text{CaCl}_2$  or  $\text{MgCl}_2$ ). All samples are measured up to between 10 and 40 min after addition of the electrolyte, with measurements of 15 s each. The initial agglomeration rates were presently not determined and the data were only examined qualitatively. The main observations are summarized in Table 3.

In  $\text{CaCl}_2$  and  $\text{MgCl}_2$  media and  $[\text{IS}] = 0.1$  M, 1 M and 3 M, the clay colloids agglomerate immediately and already significantly in the first 15 s. This is also the case in  $\text{NaCl}$  media at  $[\text{IS}] = 1$  M and 3 M. These observations are true whatever the aqueous media and their pH which indicates that the IS value is the key parameter under the conditions tested. In addition the additional presence of 2.5 mg/L FA (1.5 mg/L NPOC) does not influence the results and does not prevent the fast agglomeration of the clay colloids.

In  $\text{NaCl}$  medium at 0.1 M IS, the results are different. First, in absence of FA, the clay colloids agglomerate but with a lower rate as that observed at 1 or 3 M IS. In presence of FA, the colloids do not agglomerate anymore in four of the aqueous media tested: 1, 2, 3 and 4 (see Table 3 for details) and the agglomeration is kinetically hindered in the SGW prepared with or without  $\text{NaHCO}_3$ .

This observation is consistent with the one reported in D4.6 (Červinka in Bouby et al., 2014), working under conditions corresponding to our aqueous medium number 1 (ultra pure water alone) and testing the coagulation kinetics of clay dispersion in  $\text{NaCl}$  electrolyte in presence or not of organic matter (humic acid), see Figure 16. Accordingly, the results are very similar independently of the source of clay and organic matter.

This shows in addition that one or a combination of the other ions present in the SGW counterbalances the prevention of the clay colloids agglomeration induced by the presence of FA. Again, the presence of a small amount of calcium ion in the SGW might be thought responsible. This point calls for further investigations.



**Figure 16: Influence of humic acid (expressed as TOC) on CCC of Na-montmorillonite suspension (50 mg/l) and NaCl or CaCl<sub>2</sub> electrolyte.**

Conclusions of the fast coagulation study: whatever the aqueous media in which the clay colloids are obtained, they present the same coagulation behaviour at moderate to high IS (0.1 M, 1 M and 3 M) in NaCl, CaCl<sub>2</sub> or MgCl<sub>2</sub> electrolytes. In 0.1 M NaCl nevertheless, the coagulation rate is slowed down. The presence of FA only prevents or disturbs the clay colloids coagulation in 0.1 M NaCl but in none of the other conditions tested. Interestingly, those results are comparable with previously reported ones performed with clay colloids and organic matter of different origins.

**Table 3: Main observations during the coagulation experiments followed by PCS, yes: agglomeration detected, no: no agglomeration detected in the experimental time frame, FA effect observed: no: none, stabilization or kinetic effect**

Suspensions	pH	t=0 ∅ nm	NaCl			CaCl <sub>2</sub>			MgCl <sub>2</sub>		
			IS 0.1 M	IS 1 M	IS 3 M	IS 0.1 M	IS 1 M	IS 3 M	IS 0.1 M	IS 1 M	IS 3 M
1	6.5±0.1	280 ± 22	yes	yes	yes	yes	yes	yes	yes	yes	yes
1FA	6.4±0.1	269 ± 9	no	yes	yes	yes	yes	yes	yes	yes	yes
FA effect			stabilisation	no	no	no	no	no	no	no	no
2	6.1±0.1	255 ± 16	yes	yes	yes	yes	yes	yes	yes	yes	yes
2FA	6.2±0.1	257 ± 20	no	yes	yes	yes	yes	yes	yes	yes	yes
FA effect			stabilisation	no	no	no	no	no	no	no	no
3	6.1±0.1	431 ± 50	yes	yes	yes	yes	yes	yes	yes	yes	yes
3FA	6.2±0.1	381 ± 33	no	yes	yes	yes	yes	yes	yes	yes	yes
FA effect			stabilisation	no	no	no	no	no	no	no	no
4	8.5±0.1	307 ± 62	yes	yes	yes	yes	yes	yes	yes	yes	yes
4FA	8.4±0.1	250 ± 30	no	yes	yes	yes	yes	yes	yes	yes	yes
FA effect			stabilisation	no	no	no	no	no	no	no	no
5	8.4±0.1	320 ± 28	yes	yes	yes	yes	yes	yes	yes	yes	yes
5FA	8.3±0.1	292 ± 20	yes, reduced kinetic	yes	yes	yes	yes	yes	yes	yes	yes
FA effect				no	no	no	no	no	no	no	no
6	6.3±0.1	268 ± 30	yes	yes	yes	yes	yes	yes	yes	yes	yes
6FA	6.4±0.1	249 ± 27	yes, reduced kinetic	yes	yes	yes	yes	yes	yes	yes	yes
FA effect				no	no	no	no	no	no	no	no

## Long term study

A great number of batch samples have then been prepared from the initial 6 colloidal clay stock suspensions (Bouby et al., 2014, D4.5 and D4.6) to study the colloid stability over a long time period, at least 4 years, which means beyond the end of the project. They consist finally in suspensions at different colloid concentration (1, 5, 10 and 100 mg/L) in each of the 6 aqueous media. The influence of OM is examined in parallel by preparing the batch samples once again after adding, prior to the dilution, 2.5 mg/L fulvic acids (FA-573, Gorleben site, Lower Saxony, Germany). This represents 1.5 mg/L NPOC. The samples are stored in the laboratory (at  $\sim 21\text{-}22\text{ }^{\circ}\text{C}$ ) but preserved from the light.

Exemplarily, two of them from the set number 6, containing FA have been analysed. These preliminary investigations are reproducible and very promising. The samples were first examined prior to any shaking. The pH remains constant at respectively  $6.4 \pm 0.1$  in these two samples and they present a mean effective intensity-weighted clay colloids diameter of  $(205 \pm 16)$  nm. Shaking the samples has no influence on the pH values but significant differences in the colloid sizes are then reported, with a value  $> 310$  nm in both samples. It agrees with the colloidal concentrations measured before and after shaking which reveal a gradient. Actually the upper part of the samples is depleted in colloids with a decrease in concentration from 30 % up to 40 %. This indicates that under the experimental conditions investigated, which are representative of a glacial melt water at quasi-neutral pH (SGW at pH 6.4 and low IS), the clay colloids undergo a slow agglomeration process even in presence of OM. These measurements have to be continued systematically which will allow a very interesting comparison between different experimental conditions over a long time period.

## The improvements of mechanistic model of bentonite swelling (KTH)

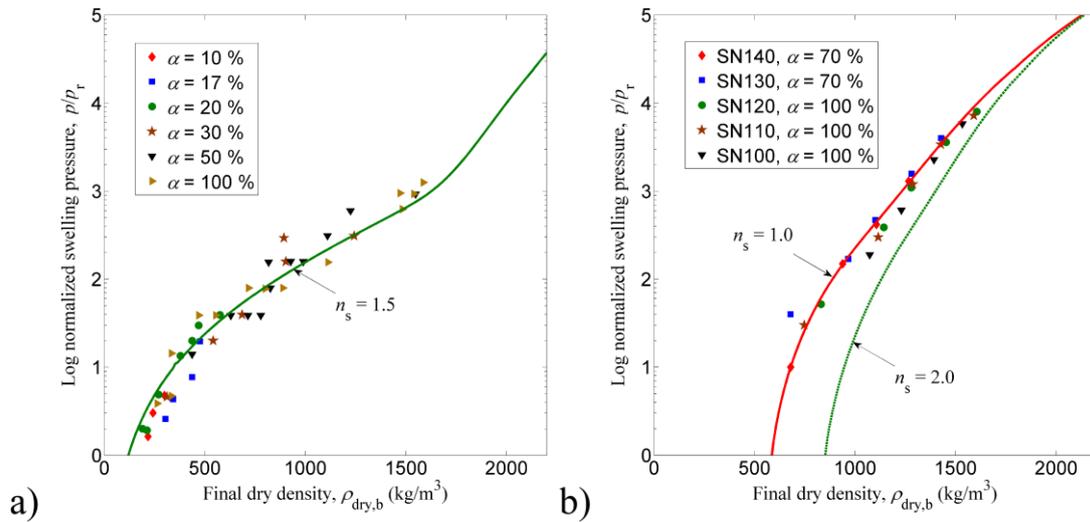
Within the BELBaR project, our group at KTH developed a mechanistic model (Liu, 2013) to predict, *at the macroscopic level*, the swelling pressure of fully saturated, bentonite-based materials in distilled water or dilute saline solutions over a large range of final dry densities of bentonite. In addition, we established a weighted correlation approach (Wang et al., 2011a; Yang and Liu, 2015) to density functional theory and used it to understand, *at the molecular level*, the interaction between charged plate-like particles in an electrolyte (Wang et al., 2011b) and in distilled water (Liu, 2015). In this section, we briefly summarize what we found from these studies (Liu et al., 2015).

### Prediction of swelling pressure of bentonites

The mechanistic model we developed (Liu, 2013) applies a thermodynamic relationship to describe the contribution of *crystalline swelling*, while using a diffuse double-layer model to

explain the behaviour of *osmotic swelling*. It accounts also for the demixing of exchangeable cations and the disintegration of montmorillonite particles into small stacks upon water uptake. The idea behind the model is that although no theory could be used to predict the stack sizes as a function of bentonite properties, the interaction between the stacks that have been formed at the end of crystalline swelling can still be described by the DLVO theory during osmotic swelling. The number of smectite sheets in the stacks depends on the types of counterions and ionic strength of the pore water, and typically varies between 1 and 10.

Comparison of the model predictions with a great number of experimental results of swelling pressures of different types of bentonites and bentonite-aggregate mixtures in both distilled water and dilute saline solutions suggests that the model works excellently in all the cases tested, as exemplified in Figure 17. It was found, in particular, that the water chemistry, the montmorillonite content, the type and amount of exchangeable cations in the interlayers are all important in determining the extent to which the montmorillonite particles are delaminated and hence the swelling behaviour of fully saturated, bentonite-based materials. The model did not, however, take interstratifications of several layer hydrates into account, but conceptualized the hydration of interlayer cations and the surface charge sites as a homogeneous process. This leads to the assumption of identical separation distances between the sheets within the montmorillonite particles, and as a result the size of the montmorillonite particles, i.e. the mean number of sheets per stack, may be somewhat underestimated, particularly for  $\text{Ca}^{2+}$  dominated bentonites.



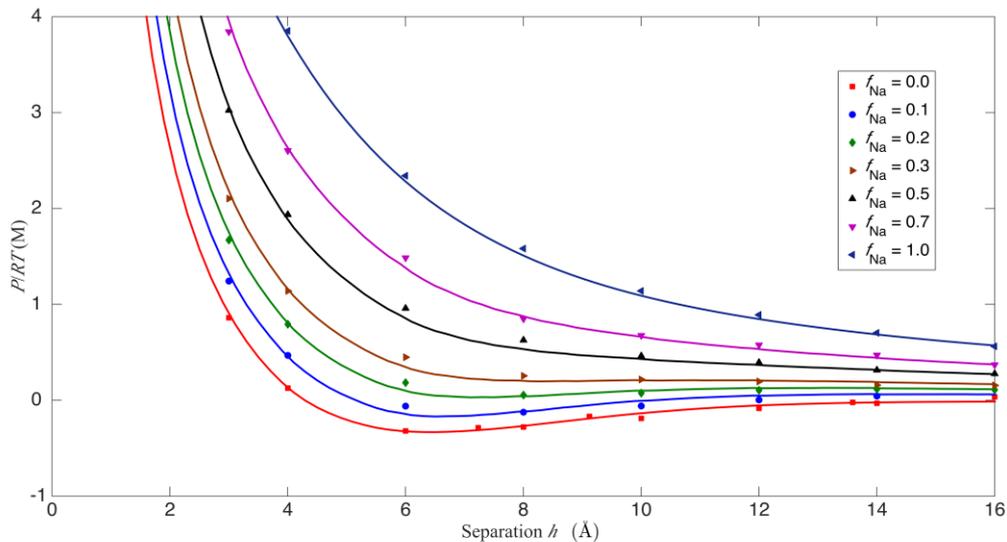
**Figure 17: Comparison of measured swelling pressure as a function of the final dry density of bentonite with the predicted pressure for a) Kunigel/sand and b) Wyr2/sand mixtures, respectively (data from Karnland et al., 2008).  $\alpha$  is the bentonite fraction in mixture, and  $n_s$  is the mean number of smectite sheets in a stack (Liu, 2013).**

As discussed in the BELBaR Deliverable D4.10 (Liu, et al., 2015), it is expected that with the use of this mechanistic model, the dynamic force balance model of Liu et al. (2009) would give a better prediction of the upward expansion of initially compacted WyCa bentonite in dilute saline solutions in a test tube, at least qualitatively, and of the erosive loss of compacted bentonite into fractures that intersect deposition holes for high-level nuclear waste.

## Understanding of interaction pressure between charged plates

Within the framework of density functional theory, we developed a weighted correlation approach (Wang et al., 2011a) to account for the cross correlations between the Columbic interaction and the hard-sphere exclusion in an inhomogeneous ionic hard-sphere fluid, by means of the concept of a weighted pair correlation function. It was shown (Wang et al., 2011a; Yang and Liu, 2015) that the ion-ion correlation effect, which was entirely neglected in the traditional Poisson-Boltzmann approach, could well be described by this approach when applied with a restrictive primitive model of electrolyte. As a result, it is superior to both the classical and the advanced approaches of density functional theory in describing the density profiles of both counter-ions and co-ions near a charged plate-like particle over a wide range of electrolyte concentrations and surface charge densities.

In particular, application of this approach to the cases of practical interest suggested that in comparison with the data of Monte Carlo simulations, it is also excellent in describing the interaction between charged plate-like particles in an electrolyte involving mono- or divalent counterions (Wang et al., 2011b), or in distilled water (Liu, 2015) where the only ions present in the electrical double layers are counterions originating from the solid-liquid interface. The results shown in Figure 18 illustrate that the competition between the counterions makes the clay always swelling in a way much like purified and fully Na-exchanged bentonites when the fraction of surface charge compensated by monovalent counterions  $f_{\text{Na}}$  is greater than 30%. The larger the Na fractional surface coverage is, the stronger the monotonic repulsion between the clay particles becomes. In the opposite situation when  $\text{Ca}^{2+}$  dominates with  $f_{\text{Na}} < 30\%$ , a shallow minimum is always present on the pressure curve leading to an attraction that favors the formation of stacks in the clay system. The less the Na fractional surface coverage is, the more sheets the stack contains, making Ca-dominated bentonites very limited in swelling. In a bentonite system with only divalent counterions, a surface charge density around  $-0.08 \text{ C/m}^2$  (not accounting for the van der Waals interaction) is sufficient to aggregate the clay particles in a face-to-face orientation into stacks incorporating a water layer of about 1.0 nm between smectite sheets.

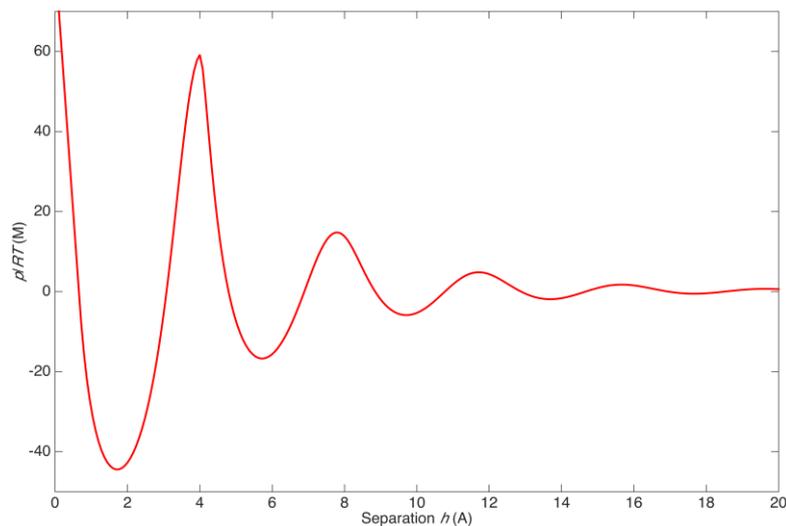


**Figure 18:** The interaction pressure between two charged plate-like particles (with a surface charge density of  $-0.11 \text{ C/m}^2$ ) as a function of separation for a salt-free system involving both mono- and divalent counterions but no coions. The diameters of the ions are assumed to be 0.4 nm. The solid markers show the results from MC simulations and the curves are from the self-consistent WCA calculations. The

**fraction of surface charge compensated by monovalent counter-ions in the electrical double layers is indicated in the figure (Liu, 2015).**

As discussed in detail in the BELBaR Deliverable D4.10 (Liu, et al., 2015), the mechanistic model (Liu, 2015) and the weighted correlation approach (Wang et al., 2011a; Yang and Liu, 2015) to density functional theory could well be applied, together with our contributions to the BELBaR Work Package 5 (Neretnieks, 2015; Neretnieks et al., 2015a; Neretnieks et al., 2015b), to improve the understanding of bentonite swelling and floc formation etc., and the quantitative models for bentonite erosion from clay buffers used to protect waste canisters and tunnels.

More recently, we extended the weighted correlation approach (Wang et al., 2011a; Yang and Liu, 2015) to include ion-water molecule and water molecule-water molecule interactions, using the solvent primitive model of electrolyte. Preliminary calculations showed that the hard-core exclusions of solvent molecules play a dominant role in determining the interaction pressure between charged plate-like particles immersed in an electrolyte solution. The strongly oscillatory force that results from the presence of the neutral solvent molecules was found to be largely independent of the properties of the electrolyte, and was not accounted for in the classical DLVO theory of colloid stability. As shown in Figure 19, this behaviour of interaction pressure is qualitatively different from that in the restricted primitive model of electrolyte where the molecular nature of the solvent is totally ignored, but consistent with experimental observations on the forces between mica surfaces in  $10^{-3}$  M KCl solution. The consequences in determining the floc formation and the interaction between spherical agglomerates in studies of dense colloidal dispersions are now under investigation.



**Figure 19: The net pressure between two charged plate-like particles (with a surface charge density of  $-0.1$  C/m<sup>2</sup>) as a function of separation for a system in equilibrium with a  $0.1$  M  $1:1$  electrolyte solution and solvent packing fraction of  $0.7$ . The diameters of the ions and the solvent molecules are assumed to be  $0.4$  nm.**

## Highlights for WP1

The main issues from WP1 are summarised in Table 4. The main outcomes / highlights from this WP4 are listed below the table in accordance with issues of WP1.

**Table 4: The main issues from WP1.**

Issue	Safety case position at start of BELBaR	Outcomes sort for final State-of-art report
<b>Synthesis of issues: Colloid stability (WP4)</b>		
<b>Colloid stability controlling processes</b>	Stability of compacted bentonite in dilute porewater conditions has been evaluated by laboratory measurements. The controlling process is hydration of exchangeable cations limited by the availability of cation free water. Currently the uncertainties in geochemical conditions are greater than in uncertainties in the stability limit. Colloid stability studies have found that model colloids that possess a significant net negative charge at neutral pH, i.e. silica and illite clay, show the greatest stability under neutral pH conditions.	Understanding of the processes controlling colloid stability and their representation in the safety case (WP4).
<b>Influence of other factors to colloid stability</b>	Accessory minerals seem to enrich near the bentonite-groundwater interface. Filtration has been discussed as a possible mean to reduce erosion. Colloid size, solution ionic strength and water flow rate are factors which strongly influence colloid migration. Association of inorganic particles with natural organic compounds is an important mechanism for colloid stabilisation. This mechanism could potentially operate to stabilise and enhance colloid populations in the near-field porewater, this remains an area of uncertainty.	Summary of the influences of these factors on colloid stability, to what extent are they significant for the safety case?

**Phase transitions of montmorillonite in DGR** – the investigations suggest that, provided the ionic strength of the ground water is above the CCC, the highly compacted clay in engineered barriers will act as a swelling repulsive paste and expand. Once the lowest clay concentration at the swelling front is below the clay concentration required for paste formation, the clay will form a gel. The lowest limit appears to be about 60 g/l, although it can be higher depending on the type of montmorillonite as well as the salinity in the surrounding system.

**Influence of bentonite properties on its stability** – one of the possible causes of the difference in the stability / erosion behaviour could be related to the different mineralogy (mainly clay minerals and its properties) of the different bentonites (tri-octahedral vs. di-octahedral clays, different exchange complex, different charge density, different charge location).

The example is that estimated CCC varies among Na-montmorillonites from different origins. Hansen and Hedström (2014) performed stability experiments at a larger number of different NaCl concentrations, give the following CCC values: Wyoming Na-montmorillonite, Wy-Na (from MX-80), 20 mM (up to 6% w/w); Milos Na-montmorillonite, Mi-Na (from Deponit

CA-N), 6-8 mM (up to 4% w/w) and for Kutch Na-montmorillonite, Ku-Na (from Asha 505), ~4 mM (up to 4% w/w).

In general, those clays having the charge located in the tetrahedral layer forms larger colloids: these particles sediment easier being less stable than others even in DW. For more details see paper in preparation (Missana et al., 2016).

**Role of anorganic compounds and (ir)reversibility of coagulation process** – changing anion has only minor effect on the CCC, provided that the anion does not directly influence the overall clay particle charge, as in the case of polyphosphates and to some extent OH<sup>-</sup>, see D4.7 (Hedström et al., 2014). Exploring the influence of interacting anions may be of less direct practical significance for the safety assessment of a repository for spent nuclear fuel, but are of utmost importance for the understanding of the chemical-physical forces that hold gels together. The effect of polyphosphates on the gelling provide evidence that the gels are formed from edge(+)-face(-) attraction.

The effect of cations (CCC) was also investigated. It has to be noted, that such tests must be evaluated taking exchange into account. Sodium and potassium, and magnesium and calcium act in similar way during the coagulation process and in real systems (e.g. natural groundwater) their effect can be simplified to the effect of M<sup>1+</sup> (Na+K) or M<sup>2+</sup> (Ca+Mg) cations, where M<sup>2+</sup> are more effective in coagulation, see D4.7 (Hedström et al., 2014) and D4.8 (Alonso et al., 2015).

The interaction of smectite with mineral like kaolinite or Al<sub>2</sub>O<sub>3</sub> produces the aggregation of particles that, alone under the same chemical conditions would be stable; this means that the presence of certain minerals not only inhibits the clay colloid generation “by dilution” of the smectite, but also may affect the properties of the smectite itself making the system unstable.

During the investigations the effect of hysteresis was observed with different methods. The rheometry measurements showed that the attractive forces in the gels increase with aging. One week of resting produce significantly stronger gels than those tested after 24 hours, see D4.9 (Hedström et al., 2015). The disaggregation process of illite and smectite clays has been shown to be not completely reversible because the aggregation process is usually very rapid (minutes) but the kinetic of disaggregation, until reaching a complete disaggregated state, largely depends on the initial conditions of the experiments. The disaggregation process is more rapid in more diluted suspensions, see D4.4 (Missana et al., 2014).

**Role of organic matter** – organic matter (like humic or fulvic acids) is able to stabilize clay colloids in NaCl electrolyte (experimental concentration up to 0.1 M NaCl). This means that in presence of organic matter more concentrated NaCl electrolyte is needed to coagulate clay dispersion (the CCC is higher). For example the CCC is four times higher in a suspension containing 0.5 mg/L TOC compared to the same suspension without humic acid, see D4.6 (Bouby et al., 2014).

In all the other electrolytes investigated (CaCl<sub>2</sub>, MgCl<sub>2</sub>) and at higher IS, the clay colloids undergo fast coagulation, independently of the presence of OM. This is true in various aqueous media containing different inorganic cations, showing that the IS remains the key parameter. In addition, calcium ions alone are able to initiate clay colloid agglomeration even at low concentrations. The presence of this inorganic cation, even at only low concentration in natural media, has thus to be taken into account.

Long term study tends to demonstrate that even under geochemical conditions where the colloids are expected to be stable, they may undergo a continuous slow agglomeration process.

**Theoretical basis and model evolution / application** – the theoretical basis for understanding of the effect of the Ca (divalent cation) on clay gel stability was nicely summarised in D4.3 (Wang et al., 2013). A self-consistent weighted correlation approximation to density functional theory was developed (Wang et al., 2011a; Yang and Liu, 2015) to describe the structural and thermodynamic properties of counterion-only electrical double layers. The predictions agree well with the Monte Carlo simulations and show that the Ca-bentonite would behave essentially as the Na-bentonite when the fraction of surface charge neutralized by Na<sup>+</sup> is more than 30 %. It is known from experiments, that this boundary lies between 20-30 %. One wish to specifically mention that crystalline swelling and stack formation of montmorillonite sheets as important factors for understanding swelling.

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