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Report on the reversibility of the coagulation process

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INTRODUCTION AND OBJECTIVES

Erosion processes and colloid generation from the compacted bentonite engineered barrier of a high level radioactive waste (HLRW) depend on the clay colloidal properties which, in turn, are strictly related with the chemistry of the system.

In the BELBaR Project, the objective of Work Package 4 (WP 4, Colloid Stability), is to understand key aspects related to colloid stability, which are needed for predicting the erosion of bentonite backfill. Clay colloid stability in aquatic environment is driven by the aquatic chemistry (ionic strength and pH) because this influences their surface charge.

In general, colloid generation is more probable when the chemical conditions favor colloid stability; on the other hand in "aggregated" systems the formation and erosion of particle in the colloidal size are not expected.

Most of stability studies that can be found in the literature deal with the analysis of the aggregation processes (sometimes with their kinetic) but much less is known on the reverse process: i.e. the "disaggregation" process. Nevertheless, to evaluate the (ir)-reversibility of colloid coagulation, when the conditions of the aqueous solution are modified to conditions favorable to stability and the kinetic of the process, is fundamental.

In the highly saline conditions of Äspö (Sweden) waters, colloid generation is almost negligible, but intrusions of diluted water (glacial melt water) may induce disaggregation. However, it is not completely clear if a system, once aggregated, can reach again a completely disaggregated state and if the kinetic of the process is reversible. Therefore, different experiments were designed with montmorillonite and illite clays to gather information on this topic.

In this report, aggregation/disaggregation processes produced by the changes in ionic strength in smectite (the main component of the bentonite backfill) and 2:1 clay, illite will be studied. In a later stage, the effects of pH changes on disaggregation processes will be evaluated.

EXPERIMENTAL CONTRIBUTIONS

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Experimental methods

All the experiments started using a reference "disaggregated" colloidal suspension, prepared in $NaClO_4$ $5 \cdot 10^{-4}$ M. This sample was then "aggregated" by ionic strength (at I=0.1 M $NaClO_4$) using the dialysis bag method or directly adding the salt. After aggregation, the electrolyte was changed several times until recovering the initial chemical conditions. The pH and conductivity of the suspension were periodically measured as well as the size of the colloids in the suspension, to obtain information on the aggregation state of the particles.

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The analysis of the size of the colloids upon changes in the water chemistry was carried out by two methods: 1) photon correlation spectroscopy (PCS) and 2) single particle counting (SPC).

PCS analyses were carried out with a Malvern 4700 system equipped with a Spectra Physic argon laser (λ= 514 nm, 1 W) and the photomultiplier located at a scattering angle of 90°. The PCS's detection limits for bentonite colloid is approximately 1 mg/L.

SPC is based on the principle of light scattering by single particles to determine concentration and size distribution. More details on SPC can be found in Degueldre et al. (1996) Rossé and Loizeau (2003). An important feature of this technique is that, in contrast to techniques like PCS, it allows the measurement of natural, highly poly-dispersed and diluted water samples.

The SPC measurements were performed with HSLIS-M50 and HVLIS C200 particles counter from PMS (Particle Measuring System, Inc.) and a photodetector (micro laser particle spectrometer, μLPS). This combination of single-particle monitors and spectrometer allows the counting of 13 size classes from 50 to 5000 nm.

HSLIS-M50 has four channels to detect particles with size between 50 and 200 nm in the size range of 50-100 nm, 100-150 nm, 150-200 nm and 200 nm.

HVLIS C200 has eight channels and measures particles between 200 and 5000 nm, in the size range of 200-300 nm , 300-400 nm, 400-500 nm, 500-700 nm, 700-1000 nm, 1000-1500 nm, 150-2000 nm, 2000-5000 nm.

The sample is injected, with a high precision volumetric pump (DESAGA KP 200) into the ultrapure water (Milli-Q from Millipore) main stream, at water flow rate of 500 mL/min. The sample is subsequently divided in two lines at water flow rate of 100 and 400 mL/min to be analyzed by the HSLIS-M50 and HVLIS C200, respectively.

Results and discussion

Disaggregation experiments with dialysis bags with Na-FEBEX smectite

The scheme of the disaggregation experiment with dialysis bag is summarized in Figure 1.

Stable Na-FEBEX smectite colloid prepared in $5\cdot10^{-4}$ M $NaClO_4$ were used as starting solution. The colloid concentration used for these tests was relatively high: 700 ppm. These colloids had an initial mean size of 270 ± 30 nm, which represent the "reference" size in the disaggregated state for smectite colloids. Colloid size in these experiments was measured by PCS.

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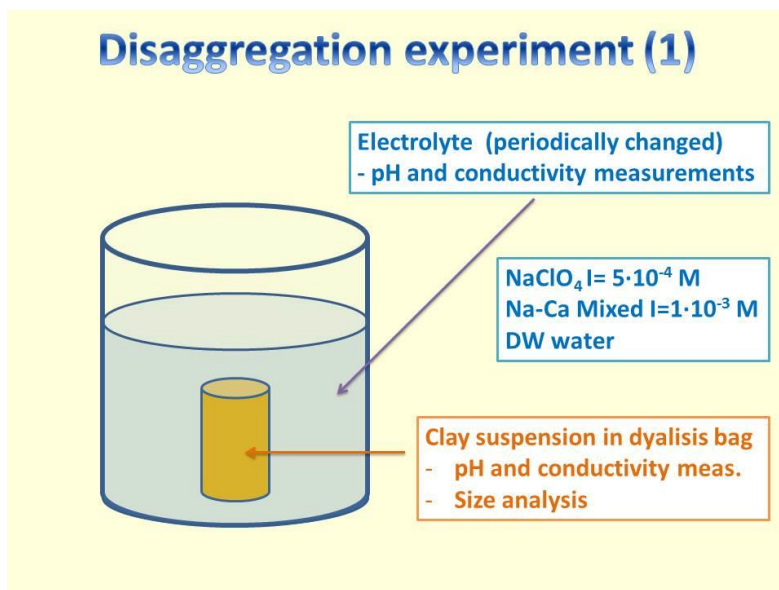Date of issue of this report: **12/06/2014**

Figure 1. Schematic of the disaggregation experiment using dialysis bags.

Approximately 200 mL of this suspension was introduced in a dialysis bag, and the bag located in a glass container. In order to produce the aggregation of smectite colloids, the container was filled with 0.1 M $NaClO_4$. Then, electrolytes of lower ionic strength were used to start colloid disaggregation. The pH and conductivity of the external solution and the suspension within the dialysis bag were measured to check when the inner and the external electrolyte were equilibrated. The external electrolyte was periodically changed until attaining the equilibrium. Two mL of the suspensions were periodically taken to measure the size of colloids. Figure 2 shows the results of this experiment. Figure 2a shows the variation of conductivity of the solution within the dialysis bag and Figure 2a the mean size of colloids.

The initial increase of the ionic strength from $5 \cdot 10^{-4}$ M to $1 \cdot 10^{-1}$ M (in Na), with an increase in conductivity of approximately 200 times, produced a very rapid increase of the colloid mean size (from 270 nm to around 2500 nm).

The disaggregation of these colloids was analyzed upon changing the external electrolyte. To obtain the disaggregation, solutions of lower ionic strength must be used. First of all, a mixed Ca-Na electrolyte (Mixed Water) with ionic strength of $1 \cdot 10^{-3}$ M, solution which simulates Grimsel water, was used; than it was changed by $5 \cdot 10^{-4}$ M $NaClO_4$ and finally by deionized water (DW).

Upon the first electrolyte change (Mixed Water), colloid size initially increased up to approximately 3200 nm; this is not surprising because even the ionic strength started to decrease, the income of calcium does not favor the disaggregation. The progressive decrease in colloid size starts to be visible when the internal and the external solutions were equilibrated with a conductivity value of 100 μScm^{-1} approximately.

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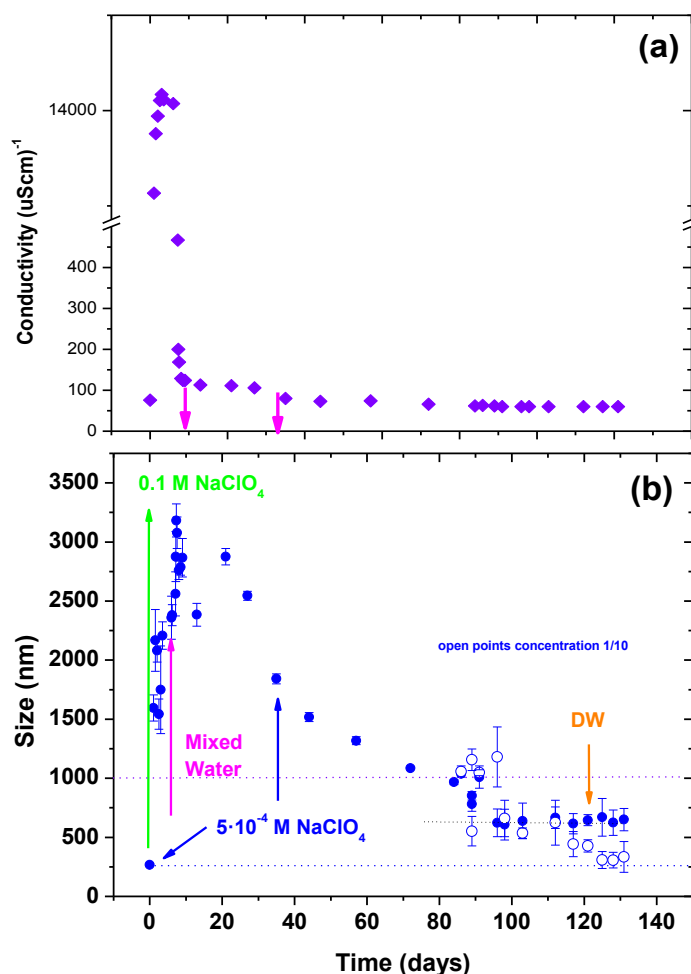Date of issue of this report: **12/06/2014**

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Figure 2: Results of the disaggregation experiment with dialysis bags with Na-Febex smectite. (a) conductivity and (b) colloid mean size measurements. pH between 5.5 and 6.5.

After approximately 40 days of the experiment, when the mean colloid size was approximately 1700 nm, the electrolyte was changed to $5 \cdot 10^{-4}$ M $NaClO_4$ coming back to the initial state. The size of colloids continued decreasing, but approximately additional 40 days were needed to reach 1000 nm.

After approximately 90 days, one aliquot within the dialysis bag was taken and diluted 1:10. Thus, a parallel experiment was carried out with the diluted suspension in a new dialysis bag (open points in Figure 2) to observe if effects due to the electrolyte concentration were visible.

The size of colloids (in both dialysis bags) reached a plateau around the day 100 of the experiment. The value of the size, around 600 nm, is about twice than the initial starting size.

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Results clearly show that even if the *"aggregation"* (for ionic strength) is a process which occurs immediately after the chemical change, *"disaggregation"* is not. In fact, after 4 months, the initial colloid size has not recovered yet.

The last step of the experiment was carried out with deionized water. Few points were taken so far. In the more concentrated suspension, after 10 days, the size remained around 600 nm, whereas it decreased up to approximately the initial size (300 nm) in the more diluted sample. This probably means that the colloid concentration is one of the parameters that can affect the disaggregation kinetic and has to be accounted for.

A similar experiment with dialysis bags was also carried out to follow the disaggregation kinetic in each state for longer time. The starting suspension was constituted by 25 ppm Na-FEBEX smectite colloids prepared in $NaClO_4$ at $5 \cdot 10^{-4}$ M (pH 6.7 and E.C = 62 µS/cm), which was aggregated changing the ionic strength to 0.1 M with $NaClO_4$ (pH = 5.47, E.C = 10500 µS/cm).

The mean size in the initial "stable" suspension was 290±30 nm which increased up to 1500 nm immediately after the increase of ionic strength.

In this case, once the inner and outer solutions were equilibrated to the required ionic strength, part of the suspension in the dialysis bag (10 mL) was taken apart, located in a separate vessel and the changes in colloid size measured in these vessel. Different samples were extracted, at equilibrium, at different stepwise ionic strengths of 0.02 M, 0.01 M, $5 \cdot 10^{-3}$ M and $5 \cdot 10^{-4}$ M. In all these disaggregated samples, the average size measured as a function of time.

Figure 3 shows the average size of samples: initial ($5 \cdot 10^{-4}$ M), aggregated (0.1 M) and at different disaggregated samples as a function of time. It can be appreciated that in $5 \cdot 10^{-4}$ M $NaClO_4$ the average size of colloidal particles slightly and slowly decreases in the disaggregated samples as a function of time, but even decreasing ionic strength to the initial values, the average size of the initial sample (290 nm) is not completely recovered.
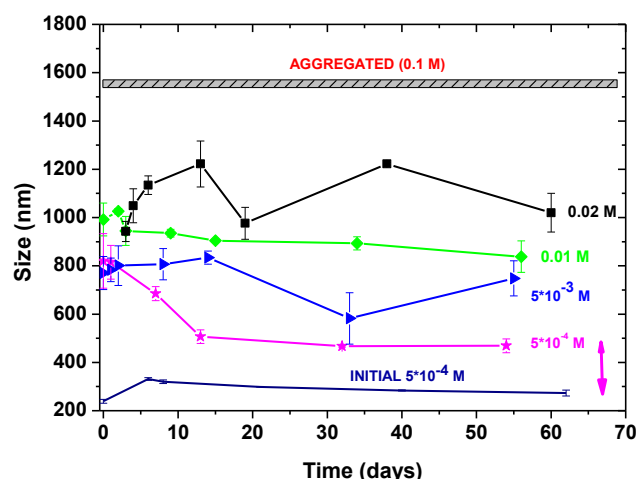

Figure 3. Average size measured by PCS on FEBEX Na-smectite in: initial, aggregated and disaggregated samples (0.02, 0.01, $5 \cdot 10^{-3}$ and $5 \cdot 10^{-4}$ M) as a function of time.

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Disaggregation experiments with Na-FEBEX smectite and Na-illite: size distribution analyses by SPC.

Aggregation experiments with Na-illite were carried out previously to compare its aggregation behavior to that of Na-FEBEX smectite (Missana and Adell, 2000). These results are described in Benedicto (2013) and, here, they will be just summarized. The zetapotential of illite colloids is negative in all the pH range (-20 to -40 mV), similarly to smectite, slightly decreasing with increasing the pH. A clear difference in zetapotential varying the ionic strength was not visible between 10^{-4} M and 10^{-2} M. This is in agreement with previous studies onto illite (Horikawa et al., 1988). The nature of the main exchange cation does not seem to affect significantly on zetapotential (comparison between natural and exchanged illite). The minimum size measured by PCS for illite particles is 278.9±3.5 nm (pH 6.2 and I=$1\cdot10^{-4}$ M in NaClO$_4$), quite in agreement with the values observed for smectite. This value can be considered as the mean size for the illite disaggregated state. The change of pH to 4.1, 6.7, 9.3 y 11.9 did not affect the mean size of the particles and the system remained stable. Similarly, an increase of the ionic strength to $1\cdot10^{-3}$ M in NaClO$_4$, did not affect the system.

However, the increase to 10^{-2} M produced a relatively slow increase of the particle mean size (991 nm in Na-illite and 743 nm in natural illite, after 25 minutes). The increment of the ionic strength, to 0.1 M produced the aggregation of the system in approximately 5 minutes (1355 nm in Na-illite and 1231 nm in natural illite), which increased up to reaching 2486 nm (pH 6-7). Rapid aggregation of the particles (1750-1800 nm, in 15 min) was also obtained at pH 2.

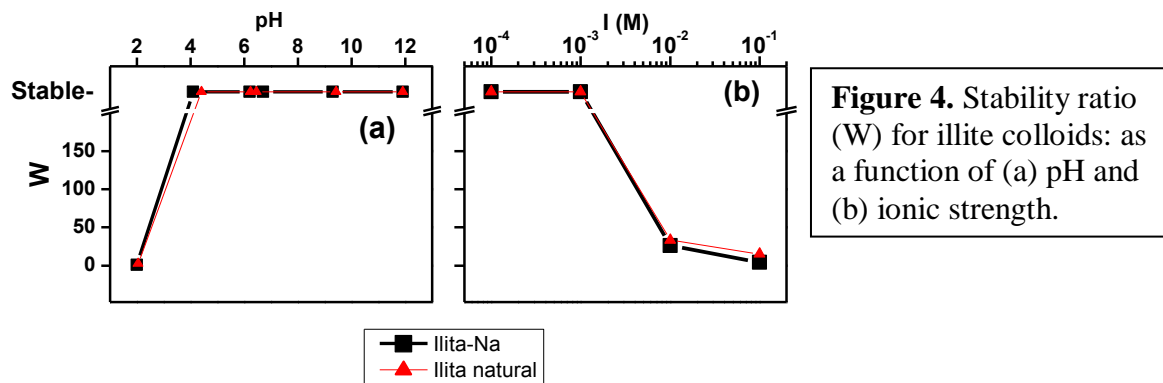The stability ratios, calculated from these coagulation experiments, are summarized in Figure 4.

Figure 4. Stability ratio (W) for illite colloids: as a function of (a) pH and (b) ionic strength.

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Both illite and FEBEX smectite previously exchanged with Na were used. In both cases, the initial pH of the samples was between 6 and 7 and the ionic strength $I=1\cdot10^{-4}$ M in $NaClO_4$. Under these conditions, both colloidal suspensions were stable and "disaggregated".

Starting from these initial suspensions, two different samples at higher ionic strength were obtained by adding 1M $NaClO_4$: the first one at $1\cdot10^{-1}$ M and the second one at $1\cdot10^{-2}$ M. The increase of the ionic strength, as already shown in previous tests, causes the aggregation of colloids, which was clearly detected by PCS by an increase of the mean particle size.

According to the coagulation experiment by PCS, the "aggregated" reference state was considered the one at $I=1\cdot10^{-1}$ M; at $I=1\cdot10^{-2}$ M the sample presented a lower level of aggregation. After the preparation, the "aggregated illite" at $1\cdot10^{-1}$ M sample was diluted to obtain 4 different samples with the same solid concentration (18.5 µg L-1) and four different ionic strengths ($1\cdot10^{-1}$, $1\cdot10^{-2}$, $1\cdot10^{-3}$, $1\cdot10^{-4}$ M); the sample aggregated at $1\cdot10^{-2}$ M was diluted to obtain two additional samples (at $1\cdot10^{-2}$ and $1\cdot10^{-4}$ M). The same was done for the Na-Febex smectite. A summary of all the samples used for disaggregation experiments with SPC is given in Table 1.

Table 1: Suspensions used in the disaggregation study by SPC

Na-illite				
	Initial		Final	
Nombre de la muestra	I_{ini} (M)	[col]ini (µg L-1)	I_{final} (M)	[col]$_{final}$ (µg L^{-1})
Reference Ili 10^{-1}	10^{-1}	18400	10^{-1}	18.5
Diluted Illi $10^{-1}\rightarrow10^{-2}$			10^{-2}	18.5
Diluted Illi $10^{-1}\rightarrow10^{-3}$			10^{-3}	18.5
Diluted Illi $10^{-1}\rightarrow10^{-4}$			10^{-4}	18.5
Reference Illi 10^{-2}	10^{-2}	18400	10^{-2}	18.5
Na-FEBEX				
	Initial		Final	
Nombre de la muestra	I_{ini} (M)	[col]ini (µg L-1)	I_{final} (M)	[col]$_{final}$ (µg L^{-1})
Reference Mont 10^{-1}	10^{-1}	50000	10^{-1}	125
Diluted Mont $10^{-1}\rightarrow10^{-2}$			10^{-2}	125
Diluted Mont $10^{-1}\rightarrow10^{-3}$			10^{-3}	125
Diluted Mont $10^{-1}\rightarrow10^{-4}$			10^{-4}	125
Reference Mont 10^{-2}	10^{-2}	50000	10^{-2}	125

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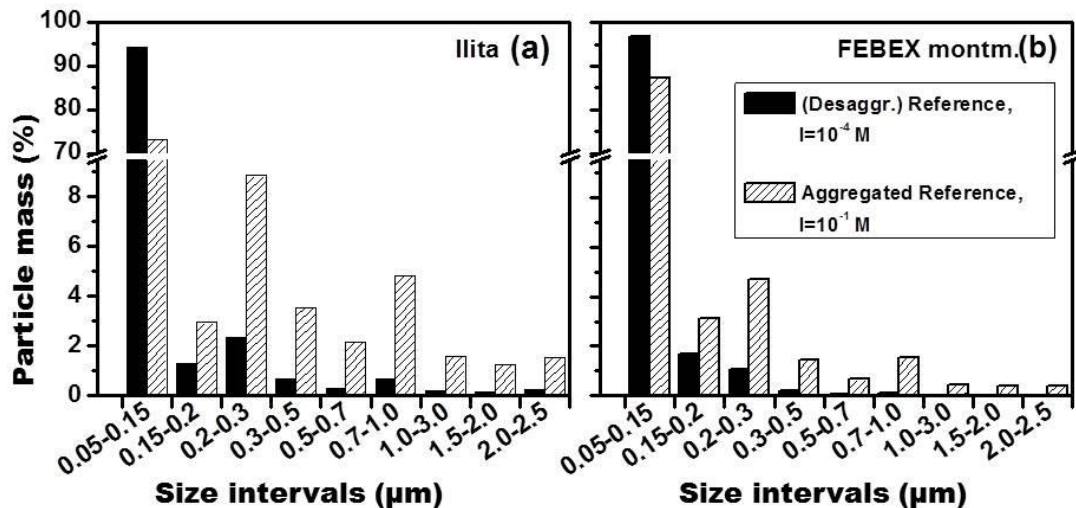Date of issue of this report: **12/06/2014**

Figure 5: Size distribution of (a) Na-illite and (b) Na-FEBEX smectite at I=10^{-1}M (aggregated reference) compared to that of I= 10^{-4} M (disaggregated). pH between 6 and 7.

One day after the preparation, these were measured by SPC to determine their size distribution. Figure 5 shows the size distribution of the "disaggregated" (I=1·10^{-4} M) and "aggregated" (1·10^{-1} M) samples. Figure 5(a) shows the results for Na-illite and Figure 5(b) for Na-FEBEX smectite. Data are expressed as percentage of colloid mass in each size interval.

In the "disaggregated" Na-illite sample, colloids of size between 0.05 and 0.15 μm represent approximately the 94% of the total mass; particles of size between 0.2 and 0.3 μm represent a 2.3% of the total mass; colloids of larger sizes present, in each size interval, fractions lower than 1% of the mass. In the illite "aggregated" sample, colloids with a size between 0.05 and 0.15 μm represent a 73% of the mass and colloids between 0.2 and 0.3 μm represent 8.9% of the mass. Percentages around 5 % are also observed in size intervals corresponding to larger particles.

Qualitatively similar results were observed also for the Na-Febex smectite which, at I= 10^{-4} M, presents a 97% of mass in the smallest size range (higher than that of illite under the same conditions); the "aggregated" Na-Febex sample presents the 87% of the colloids between 0.05 y 0.15 μm.

Considering the SPC result, a large quantity of particles remains disaggregated even at high ionic strength. Measurements PCS lead to a mean size of approximately 300 nm for "disaggregated" samples and higher than 1 μm for aggregates ones. In PCS measurements, large particles tend to mask the presence of the smaller ones, which might be one of the causes of the (apparent) differences between PCS and SPC measurements.
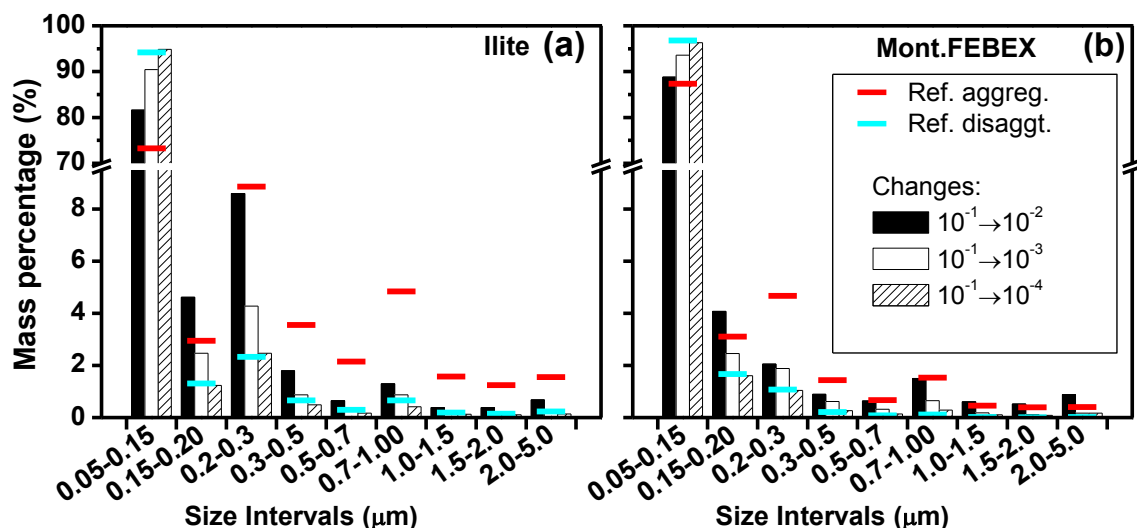
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Figure 6: Disagreggation of (a) Na-illite and (b) Na-Febex smectite after 24 h: from I= 0.1 M to different ionic strengths (pH 6-7). Red line represent the values previously obtained of the "aggregated" reference sample (0.1 M) and the cyan line those for the "disaggregated" one ($1 \cdot 10^{-4}$ M).

Furthermore, colloid concentration necessary to perform the experiments with the two techniques is quite different. The concentration of colloid experiments with SPC, is generally much smaller than that used in PCS and the aggregation is expected to increase with the concentration increasing the probability of particle collision (O'Melia, 1995); (Friedlander, 2000). Furthermore, during the measurement the sample to be analyzed is diluted in the deionized water flow which can more rapidly trigger the disaggregation process.

Therefore it has to be accounted for that, the measurements conditions of both techniques might not be completely comparable and data interpretation has to be made considering these differences.

The samples in which the ionic strength was decreased after aggregation were also analyzed by SPC, one day after their preparation. Figure 6 shows the size distribution of the colloids 24 hours after the change in ionic strength from I=0.1 M to 10^{-2}, 10^{-3} and 10^{-4} M for (a) Na-illite and (b) Na-FEBEX smectite, indicating the different aggregation states upon the ionic strength decrease. It can be observed that the percentage of colloidal mass for Na-illite in the size range of the smaller particles increases (82%, 90% y 95% in 10^{-2}, 10^{-3} y 10^{-4} M respectively) whereas the percentage of colloidal mass in the range of the particles between 0.2 and 0.3 μm decreases (8.6 %, 4.3%, 2.5%). In the particle size range between 0.7 and 1 μm values of 1.3 %, 0.9% and 0.4% for 10^{-2}, 10^{-3} and 10^{-4} M, were found. The same tendency is seen for the Na-FEBEX smectite.

The sample in which the ionic strength returned to at 10^{-4} M is similar to the initial "disaggregated" one. Thus under these experimental conditions, after 24 ours the sample has disaggregated.
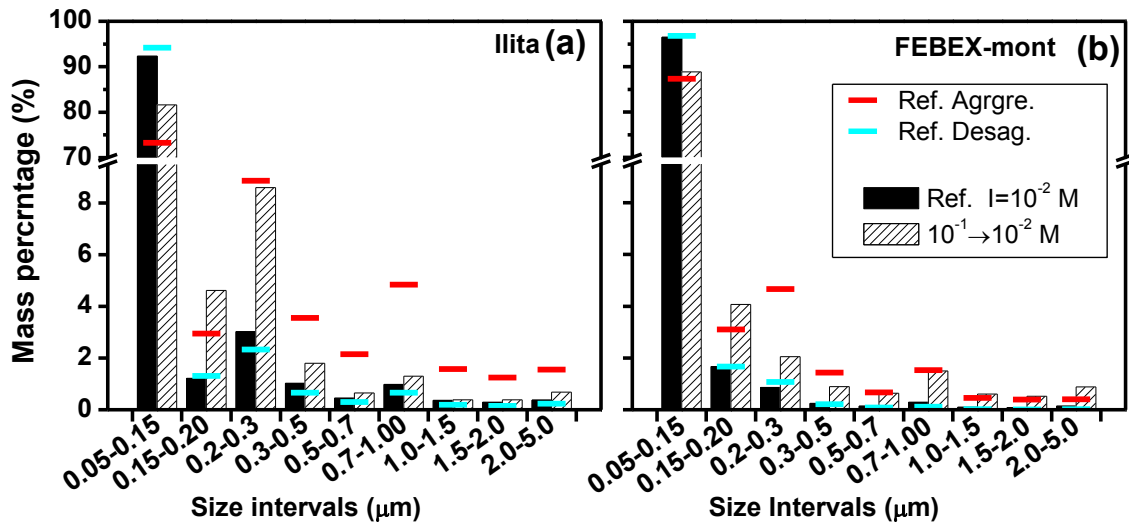
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Figure 7: Comparison of the size distribution of the sample prepared from I=1·10^{-4} M to I = 10^{-2} M (reference) and the other brought from I=0.1 M to I=1·10^{-2} M (previously aggregated). (a) Na-illite and (b) Na-FEBEX smectite.). Red line represent the values previously obtained of the "aggregated" reference sample (0.1 M) and the cyan line those for the "disaggregated" one (1·10^{-4} M).

Figure 7 shows the size distribution for (a) Na-illite and (b) Na-FEBEX smectite, of two suspension at 1·10^{-2} M; the first one prepared from the reference disaggregated sample (1·10^{-4} M) and the other from the aggregated one (1·10^{-1} M) 24 hours after its preparation.

The first sample (reference) presents a 92% of the mass in the interval between 0.05 and 0.15 µm, whereas the initially aggregated suspension presents only the 81% of the mass in this interval. Disaggregation has occurred with respect to the sample at 0.1 M but, in 24 hours, this time the disaggregation process has not been complete. The same was seen for the Febex smectite.

The kinetic of the process seems to depend on the initial and final conditions. More diluted waters seem to favor the reversibility of the process.

As future work, it is foreseen to perform similar experiments producing colloid aggregation by changing the pH.

Conclusions

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. However, at a long-term, it is possible that the recovery of the initial state would be total. Very favorable electrolytes like deionized water accelerate the process whereas in mildly saline electrolyte hysteresis is observed. The concentration of colloids is also another point to be taken into account. The disaggregation process is more rapid in more diluted suspensions.

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The reversibility of the aggregation for changes in pH has to be investigated as well as the role of divalent ions on disaggregation kinetics.

Acknowledgements

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