



BELBaR

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**Effect of pH on clay colloid stability: present
experimental work based on previous studies**
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1 Introduction

The stability of bentonite colloid suspensions is critical to assess their role in radionuclide transport.

The main mineral composing bentonites is montmorillonite, which is a 2:1 layer (2 tetrahedral and 1 octahedral) clay. The main contribution to the surface charge in these clay minerals is permanent and it is due to isomorphic substitutions within their layer structure. In these layers, atoms of lower valence usually replace atoms with higher valence, leading to an excess of negative charge, which is compensated by the presence of cations near the surface. At the edge of the clay particles, where the primary bonds of the tetrahedral and octahedral layer are broken, an electric double layer is formed by the adsorption/desorption of hydroxyl ions. This produces an additional pH-dependent contribution to the surface charge. Since the stability behavior of a colloidal suspension is closely related to the surface charge properties of the suspended solid, the contribution of both the permanent and pH-dependent charge should be considered when stability predictions for clay materials are carried out (Missana & Adell, 2000).

To determine the point of zero charge is essential in coagulation studies, and it is mostly evaluated by measuring the electrokinetic mobility as a function of salt concentration and pH (Lyklema, 1984, 1995).

Stability studies analyse whether or not clay colloids aggregate as function of several chemical and physical parameters, such as pH, ionic strength, presence of different multivalent ions, organic ligands or temperature and have been largely investigated in clay colloid science (Lagaly, 2006; Rien, 2011).

The coagulation kinetics is analysed by different techniques that determine the particle diameter, as for example by time-resolved dynamic light scattering technique using Photon Correlation Spectrometry (PCS) (Novich & Ring, 1984). The influence of cations on colloid stability is also evaluated considering the critical coagulation concentration (CCC), as the minimum concentration that at which colloids start to aggregate (Lagaly & Ziesmer, 2003).

Many stability studies of clay colloids as a function of different parameters, and in particular of pH are available in the literature (i.e. Tombacz et al, 1999; Tombácz & Szekeres, 2004). Wyoming bentonite is the most studied clay. For example, critical coagulation concentration (Lagaly & Ziesmer, 2003; García-García et al, 2007), bentonite colloid stability were analysed (García-García et al, 2006; 2009), temperature effects or presence of organic ligands (Permien & Lagaly, 1994) was analysed for Na- Wyoming bentonite. Rheological properties as a function of pH were studied (Kelessidis, et al, 2007). Stability of Mx-80 bentonite in different saline waters from pH 7 to 9 (Lahtinen et al, 2010) was analysed. Clay colloid structure analyses can be found in (Morris & Zbik, 2009; Fernández et al, 2013).

Stability of FEBEX bentonite colloids was studied as well, as function of pH and ionic strength (Missana & Adell, 2000; Missana et al, 2003) and in different groundwaters (Kunze et al., 2008; Bouby et al, 2011). Stability studies as a function of pH for other bentonites are scarce.

This report presents the colloid stability studies carried out within BELBAR project by different institutes. The long-term colloid stability studies carried out by KIT-INE, the study of Czech bentonite as a function of different organic ligands carried out by ÚJV Rež. The stability studies as a function of pH and ionic strength carried out by CIEMAT on five different bentonites (FEBEX, Mx-80, Mylos, Czech B75 and Russian bentonites).

2 KIT-INE experiments on colloid stability.

According to previous work (Bouby et al, 2011), performed over a 3 years period, the clay colloids undergo a continuous agglomeration process even in natural ground water where conditions were first thought to be ideal for clay colloid stabilization. The water chemistry and mainly the Ca^{2+} concentration determine the colloid size distribution.

In more details, the asymmetric flow field-flow fractionation (AsFIFFF) combined with various detectors like an ICP-MS was applied to study size variations of colloids. The colloids suspended directly in the low ionic strength (I), slightly alkaline granitic groundwater ($I = 10^{-3} \text{ mol/L}$, $\text{pH} = 9.6$) of the Grimsel Test Site (GTS, Switzerland) showed a gradual agglomeration with a size distribution shift from initially 10 - 200 nm to 50 - 400 nm within over 3 years (see Figure 1).

The Ca^{2+} concentration of $2.1 \cdot 10^{-4} \text{ mol/L}$ in the Grimsel ground water is believed to be responsible for the slow agglomeration due to Ca^{2+} ion exchange against Li^+ and Na^+ at the permanently charged basal clay planes. Furthermore, the Ca^{2+} concentration lies close to the critical coagulation concentration (CCC) of $10^{-3} \text{ mol L}^{-1}$ for clay colloids. Slow destabilization may delimit clay colloid migration in this specific groundwater over long time scales.

This result was partly supported by the analysis of a 10 years old clay colloid suspension preserved in Grimsel ground water for which the final pH decreased over time and lies finally at 8.0. The combined SEM-EDX and AsFIFFF-ICPMS analysis revealed the presence of big agglomerates in addition to colloids of $\sim 200 \text{ nm}$ (60 % of the mass recovered) as seen in the Figure 2.

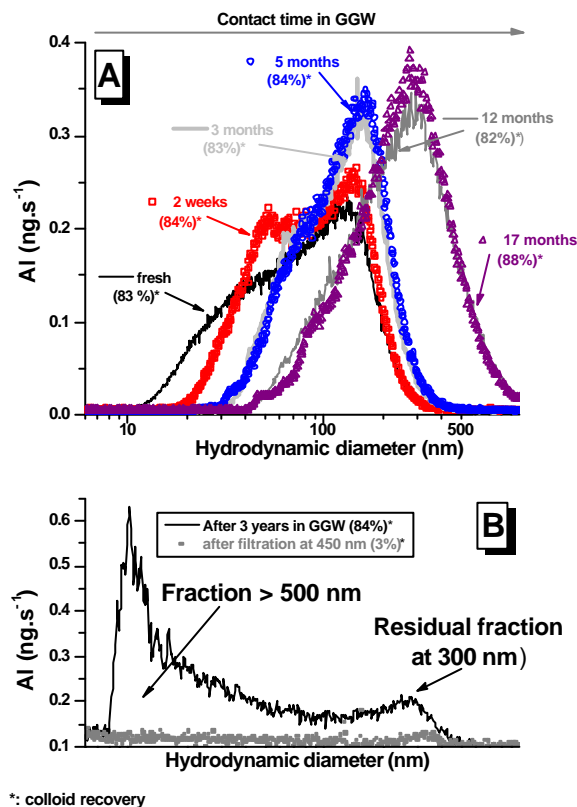


Figure 1. Evolution of Al-fractograms (representing bentonite colloids) over 3 years. The error for peak position reproducibility is less than 5%. The recoveries (values indicated in brackets) are reproducible within less than 10% uncertainty. These uncertainty ranges hold for all fractograms. (A) The AsFIFFF works in the so-called normal mode where the smaller colloids are eluted prior to bigger ones. The calibration is valid up to 510 nm. (B) The AsFIFFF works in the so-called steric mode where the bigger colloids (fraction > 500 nm) are eluted prior to smaller ones (residual fraction at 300 nm).

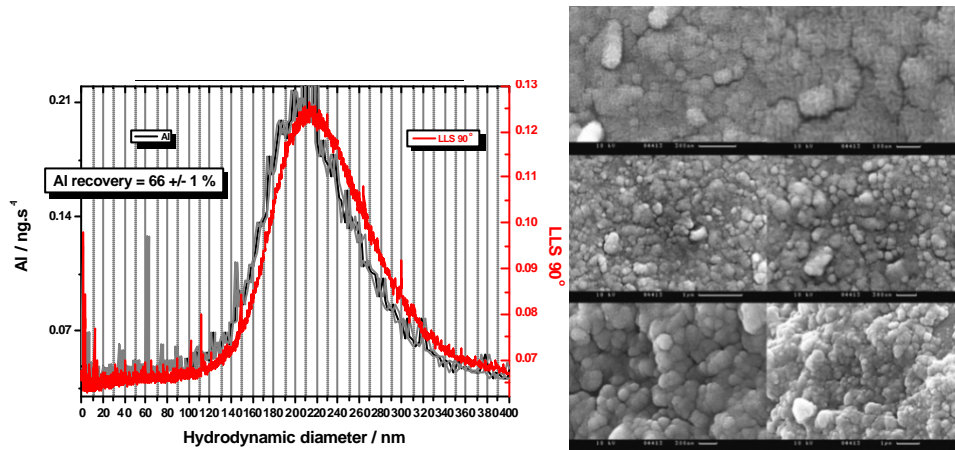


Figure 2: AsFIFFF-ICPMS/ LLS fractograms and SEM-EDX pictures obtained from a 10 years old bentonite colloid suspension in Grimsel ground water, final pH 8.0.

Accordingly, the clay colloids are more or less prone to agglomeration at high pH (8-9) under low ionic strength conditions. The aim of the new experimental work program is to examine in more details the agglomeration process.

The MX80 bentonite colloid stability is examined under glacial melt water conditions starting from a delaminated bentonite clay suspension, as in our previous work (Bouby et al, 2011). After 1 week in LiCl 1 M, the suspensions are centrifuged, rinsed and resuspended in the different media simulating the natural waters at low ionic strength ($IS = 1.3 \cdot 10^{-3} \text{ M}$): ultrapure water at pH ~6, synthetic carbonated water at pH 8.5, ultrapure water with NaCl ($1.3 \cdot 10^{-3} \text{ M}$) at pH ~ 6, ultrapure water with CaCl₂ ($0.433 \cdot 10^{-3} \text{ M}$) at pH ~ 6, ultrapure water and NaHCO₃ (10^{-3} M) at pH ~ 8.5, synthetic water at pH 5.

The colloidal suspensions obtained after the fourth centrifugation/rinsing/resuspension step are the stock suspensions. They are characterized in details after their preparation (ion compositions, colloidal concentration, colloidal size) and over time.

The colloid stability will be studied over a long time period, starting in June 2013 up to at least the end of the project. The influence of organic matter (OM) and Fe are examined in presence or not of tetravalent elements. In addition to this slow coagulation study, the fast coagulation rates will be determined in presence or not of OM.

Analytical techniques used are:

- Sieving, centrifugation
- IC, ICP-OES, ICP-MS (elemental compositions)
- PCS, SPC, LIBD, AsFIFFF-ICP-MS (size evolution and CCC)

3 ÚJV Rež studies on coagulation of clay dispersions by inorganic cations.

Basic coagulation of clay dispersions by inorganic cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) was studied. The main aim of the following experiments was to establish the critical coagulation concentrations of these cations (CCC). Essentially, CCC is the minimum concentration of coagulant (in this case cation) that causes rapid coagulation. Knowing CCCs enable to decide about stability of clay dispersions in a given

ground water (or experimental water based solution) and it is an input for further experimental work in other work packages.

As a clay material the Rokle bentonite was selected. Naturally, the Rokle bentonite (Rokle deposit, Tertiary neovolcanic area, NW Bohemia, CZ) is Ca-Mg bentonite representing by a complex mixture of (Ca,Mg)-Fe-rich montmorillonite, micas, kaolinite and other mineral admixtures (mainly Ca, Mg, Fe carbonates, feldspars and iron oxides). The bentonite is processed on the production line (grinding, homogenization) and the final commercial product (partly Na-activated) is denoted as Bentonite 75 (B75). Initially, we wanted to start with well defined material and thus the experimental work started with purification of B75.

3.1 Bentonite purification

At first the carbonates were removed by sodium acetate-acetic acid buffer, followed by iron removal using sodium dithionite in acetic acid buffer and washed by NaCl. Clay fraction < 2 µm were obtained by sedimentation in enough amount of distilled water. Next step was transfer to homoionic Na⁺ form by treatment with NaCl and washing with distilled water. Dialysis as a last step was performed until the conductivity of solution was > 10 µS/cm. The final product was air dried or lyophilised (freeze drying). X-ray diffraction confirmed the removal of carbonates, cristoballite and part of quartz. Measurement of exchangeable cations affirmed the sodium dominance in interlayer space (average equivalent fraction: Ca - 0.23, Mg - 0.09, Na - 0.63, K - 0.02).

From this powder the suspension of purified bentonite B75 and distilled water was prepared for coagulation experiments with concentration 0.1, 1 and 10 g/L. Initially, the mean hydrodynamic diameter of bentonite particles in suspensions was about 500 nm. The measurement was performed by photon cross correlation spectroscopy (PCCS) at Nanophox instrument (Sympatec GmbH, Germany).

3.2 Coagulation experiments

The bentonite colloids stability was investigated for the purified B75 present in sodium form. The CCC of univalent cations (Na⁺, K⁺) and divalent cations (Ca²⁺, Mg²⁺) were determined in the series of test-tube coagulation tests for three bentonite suspension concentrations (initial bentonite suspensions in distilled water were half diluted by electrolytes to final concentration: 0.5%, 0.05% and 0.005% w/w, i. e. 0.05, 0.5 and 5 g/L) and different electrolyte (NaCl, KCl, CaCl₂ and MgCl₂) concentrations. The visual inspection was performed after more than 48 hours and later. For more precision the inspection using laser light beam was used. Finally the presence/absence of particles in the upper part of dispersion was confirmed by PCCS measurement. The obtained CCC for individual cations and bentonite suspensions are summarised in Table 1.

Table 1: Obtained CCC values for individual cations and three bentonite suspensions. The pH values are ranges for given test-tube tests measured in suspensions after the experiments.

Component	CCC for selected cations								
	0.5 % w/w			0.05 % w/w			0.005 % w/w		
	mg/L	mmol/L	pH	mg/L	mmol/L	pH	mg/L	mmol/L	pH
Na	138-161	6-7	6.71-6.79	138-161	6-7	6.50-6.85	115-138	5-6	6.30-6.45
K	157-196	4-5	6.46-6.90	117-157	3-4	6.39-6.75	78-117	2-3	6.10-6.34
Ca	40-50	1-1.25	6.28-6.84	40-50	1-1.25	6.50-6.85	4-20	0.1-0.5	6.52-6.67
Mg	12-24	0.5-1	5.97-7.38	12-24	0.5-1	6.43-6.82	2-12	0.1-0.5	6.16-6.74

For Na⁺ the CCC was found to be in the range 6-7 mmol/L for 0.5% w/w suspension and decrease to 5-6 mmol/L for 0.005% w/w suspension. The CCC for K⁺ was found to be slightly shifted to lower concentrations and lies in the concentration interval 4-5 mmol/L for 0.5% w/w suspension and decrease to 2-3 mmol/L for 0.005% w/w suspension. The CCC for divalent cations are lower, 1-1.25 mmol/l for Ca²⁺ and 0.5-1 mmol/l for Mg²⁺ in 0.5% w/w suspension and decrease to 0.1-0.5 mmol/L for Ca²⁺ and Mg²⁺ for 0.005% w/w suspension (see Figure 3).

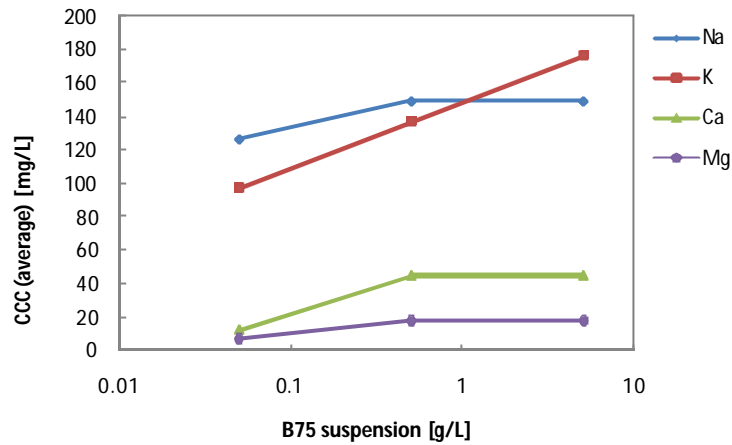


Figure 3. Variation of the CCC with the concentration of bentonite suspensions for selected cations.

The effect of increasing CCC with solid content (concentration of bentonite in suspension) is known. Generally, the interactions between surfaces are described by the DLVO theory, which takes into account the interactions between diffuse double layer (DDL) and van der Waals forces. The van der Waals attractive forces are quite independent of the electrolyte concentration in the solution over against double layer electric field. When the salts solely regulate the thickness of the diffuse ionic layer, CCC is independent of the solid content of the dispersion. However, CCC increases with solid content when the counterions are adsorbed at the surface, as they are in the Stern layer (DDL) (Bergaya et al., 2006).

Comparison of obtained CCC values of selected uni and divalent cations for all suspension of B75 in simple electrolytes were found to be significantly higher than the concentrations of appropriate cations in the SGW except Ca and Mg for 0.005% w/w suspension (compare Table 1 and Table 2). In the case of univalent cations, the observed CCC are more than one order of magnitude higher than the appropriate concentration in groundwater. In the case of calcium and magnesium (0.5% and 0.05% w/w suspension), the CCC was found to be only approx. two times higher than the concentration in groundwater. For the 0.005% w/w suspension, which equals to 50 mg/L, the CCC are lower than the concentrations of Ca and Mg in ground water. This clay dispersion will not be stable and clay particles will form aggregates.

This finding is important for future experimental work, because the concentration of Ca and Mg in the solution may be influenced by the presence of calcite and gypsum present in bentonite or rock material. It has to be noted that presented results are valid for the purified B75 converted to sodium form.

Table 2. Composition of synthetic granitic water (SGW) representing ground water from czech granitic environment and also liquid phase for further experiments.

Component		Na	K	Ca	Mg	F	Cl	SO ₄	HCO ₃	NO ₃
Concentration in SGW	mg/l	10.642	1.8	27.001	6.405	0.2	42.403	27.704	30.412	6.3
	mmol/l	0.463	0.046	0.674	0.264	0.011	1.196	0.288	0.498	0.102

4 CIEMAT experiments on colloid stability.

The stability of colloid suspensions of different bentonites was studied as a function of the pH by combining electrophoretic measurements, allowing determining the surface potential of the clay particles (Zetapotential) and Photon Correlation Spectrometry (PCS) that allows establishing the mean size of the particles under different conditions.

4.1 Experimental

Zeta potentials were determined by Laser Doppler electrophoresis with a Zetamaster Malvern system equipped with a Spectra-Physics 2mW He-Ne laser ($\lambda = 633 \text{ nm}$).

PCS analyses were carried out with a Malvern 4700 system equipped with a Spectra-Physics 4W argon laser ($\lambda = 514 \text{ nm}$) and the photomultiplier located at a scattering angle of 90° and the signal transmitted to a Malvern 7032 Multi-8 auto-correlator.

Different clays were analysed: FEBEX bentonite from Spain (Huertas et al, 2000), Mylos bentonite from Greece, Wyoming MX-80 bentonite (Müller-Vonmoos & Kahr, 1983), Czech Rokle bentonite Na-activated (B75) and a Russian bentonite from the Katasshia deposit (Sabodina et al, 2006).

For colloid preparation, the bentonites were purified and homoionized with sodium by washing it three times with 1 M NaClO_4 . The suspensions were left from 3 to 8 hours in this high strength solution to allow the complete exchange with Na. After the last washing, the suspension was decanted and deionized water was added. The colloidal fraction, with a size smaller than 500 nm, was obtained by centrifuging the suspension at $600 \times g$ for 10 min and collecting the supernatant. This procedure was repeated several times (15-20), after additions of fresh deionized water. Then, colloids were equilibrated by dialysis with NaClO_4 electrolyte at the desired ionic strength. The concentration of the initial suspensions was determined by gravimetric measurements, drying in an oven for 48 hours at 105°C three aliquots of 20 mL and weighing the dried solids.

4.2 Results

Figure 4 shows the zeta potential as a function of the pH for the suspension of FEBEX, Mylos and MX-80 colloids suspended in NaClO_4 $5\text{E-}04 \text{ M}$. Two different colloid concentrations were analyzed 25 ppm (Figure 4, left) and 100 ppm (Figure 4, right).

For all these clays, the zetapotential values are similar and around -35 mV ; the maximum variations observed are within 15 mV, most probably due to experimental variability of the measurements. The variation of the zetapotential with pH is negligible, even if for MX-80 and FEBEX, after pH 8, a slight decrease of the potential is observed.

Figure 5 shows the zetapotential as a function of the pH for the FEBEX (left) and Mylos (right) bentonites at two different ionic strengths ($5\text{E-}04$ and $1\text{E-}01 \text{ M}$). The difference observed at the two different ionic strengths are not very large (15 mV at the most), even if it seems that zetapotential decreases with increasing the ionic strength.

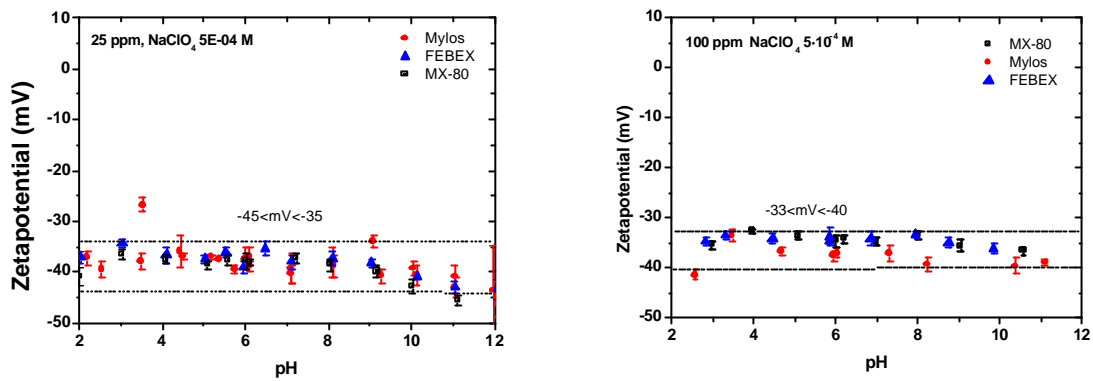


Figure 4: Zeta potential as a function of the pH for FEBEX, Mylos and MX-80 bentonites in NaClO_4 5×10^{-4} M. Left: colloid concentration 25 ppm; Right: colloid concentration 100 ppm.

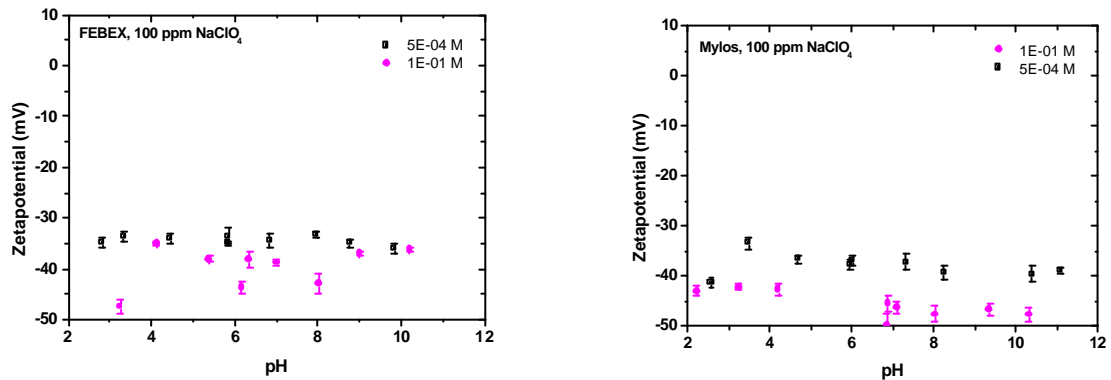


Figure 5: Zeta potential as a function of the pH for FEBEX (left) and Mylos (right) NaClO_4 5×10^{-4} and 1×10^{-1} M. Colloid concentration 100 ppm.

In order to verify this result, the zeta potential was measured in the same sample, increasing progressively the ionic strength, starting from the initial suspension in NaClO_4 5×10^{-4} M. Figure 6 shows the data obtained with Mylos bentonite. Figure 6 (left) shows the zeta potential measured increasing the concentration of Na and Figure 6 (right) shows the zeta potential measured adding Ca to the system.

Figure 6 (left) shows an effective decrease with increasing Na concentration in the system, on the other hand, the addition of calcium increase the value of zeta potential. This could be attributed to the application Smolukowski approximation to calculate the zeta potential from electrophoretic measurements (Williams & Williams, 1978).

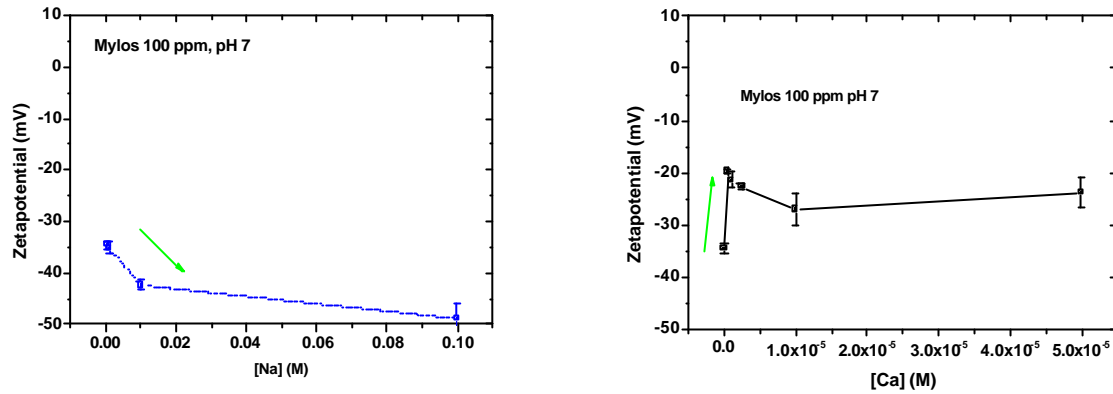


Figure 6: Zetapotential as a function of the ion concentration in the system. The starting suspension is composed by 100 ppm of Mylos colloids in 5E-04 M NaClO₄. Left: progressive addition of Na; right: progressive addition of Ca. Colloid concentration 100 ppm.

Figure 7 shows the Zetapotential as a function of pH for the Czech B75 (left) and Russian (right) bentonites at different ionic strengths. In the case of the B75 bentonite, the values are also around -35 mV, constant in the all range of pH (slightly increasing for pH lower than 5). Also in this case, at the ionic strength of 1E-01 M, values are slightly lower. In the case of the Russian bentonite zetapotential values are more dispersed (from -20 to -50 mV) and a more complex (apparent) dependence on pH and ionic strength

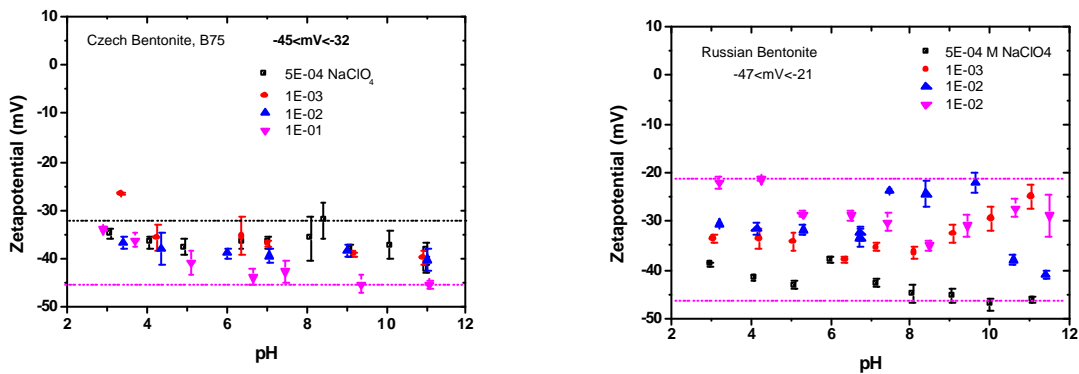


Figure 7: Zetapotential as a function of pH for the Czech (left) and Russian (right) bentonites at different ionic strengths. Colloid Concentration 25 ppm.

Figure 8 shows the size of colloid measured as a function of pH and at different ionic strengths for the five studied bentonites (A) FEBEX, (B) Mx-80, (C) Mylos, (D) Czech B75, (E) Russian bentonites.

The initial size of bentonite colloids in NaClO₄ 5E-04 M is 309 ± 5 nm for FEBEX bentonite, 310 ± 9 nm for Mx-80, 319 ± 10 nm for Mylos bentonite, 210 ± 10 nm for the Czech B75 bentonite and 270 ± 10 nm for the Russian bentonite.

For all studied bentonites, the size remains practically unvaried up to I=1E-03 M even if it slightly increases for pH lower than 4 are observed.

At $I = 0.01$ M, in the case of the Russian bentonite (Figure 8E) similar sizes (300-400 nm) are observed compared to lower ionic strengths (data are, in general, more scattered) with a visible increase for pH lower than 5. At $I=0.01$ M the mean size increases around 400 nm for the Czech bentonite (Figure 8D), 600 nm for FEBEX and Mylos bentonite and up to 800 nm for Mx-80 bentonite. There is always a mayor increase of size for pH lower than 5. In all cases, at $I=0.1$ M, colloids are completely destabilized with size outside the colloidal range.

Also in this case, at $I=0.1$ M, colloids are completely destabilized with size outside the colloidal range.

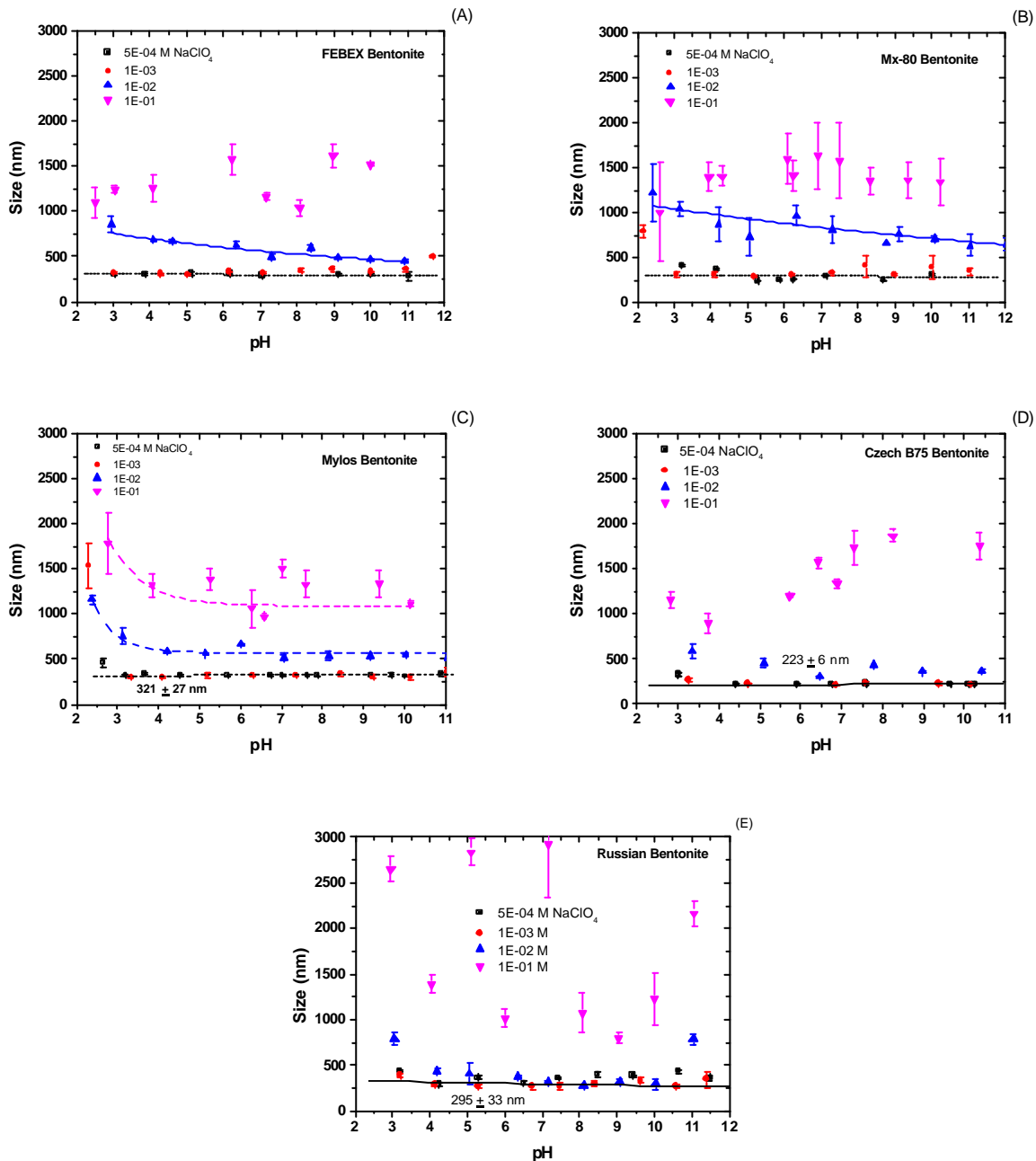


Figure 8. Size of colloid measured as a function of pH and at different ionic strengths for (A) FEBEX, (B) Mx-80, (C) Mylos, (D) Czech B75 , (E) Russian bentonites.

4.3 Conclusions of CIEMAT experiments

The stability of five different bentonites from different origin (FEBEX, Mx-80, Mylos, Czech B75 and Russian) was studied as function of pH and ionic strength by means of zeta potential and PCS measurements.

For all these clays, the zeta potential values are similar and negative -35 mV; with only slight variations at higher ionic strength, slightly different in the case of Russian bentonite

The initial size of the particles measured at lower ionic strength ($5 \cdot 10^{-4}$ M) in NaClO_4 M electrolyte was maintain almost the whole pH range in all studied bentonites up to $I = 0.01$ M. At $I = 0.01$ M colloids start to aggregate, being the effect more pronounced at $\text{pH} < 5$. In all cases colloids are destabilized, and out of colloid size for $I = 0.1$ M.

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