

COMPARISON OF THE STABILITY BEHAVIOR OF COLLOIDS OBTAINED FROM DIFFERENT RAW BENTONITES AND CLAYEY MATERIALS OF INTEREST IN THE FRAME OF HIGH-LEVEL WASTE REPOSITORIES

Tiziana Missana, Ursula Alonso, Anamaría Fernandez, Trinidad López

CIEMAT, Department of Environment, Avenida Complutense, 40- 28040 MADRID (Spain). E-mail: tiziana.missana@ciemat.es

INTRODUCTION

The analysis of the chemical conditions that make stable or unstable a colloidal system is important because the conditions that favor colloid stability are also expected to favor colloid transport and erosion processes. The intrinsic physico-chemical properties of the clay may play a role in colloid formation, dispersion, stability and, in the end, on the erodibility of the bentonite barrier.

MATERIALS & METHODS

Five raw bentonites were selected (See CIEMAT Poster by Fernandez et al., this session): FEBEX from Spain; IBECO from Mylos (Greece); Wyoming MX-80 from USA ; Czech Rokle bentonite Na-activated (B75) and a Russian bentonite from the Khakassia deposit (MSU). Data were compared with a commercial pure Na-montmorillonite (NANOCOR).

Clays (1 g/L) were dispersed in deionized water (DW). The colloidal fraction was extracted by centrifuging 600 g during 10 minutes. The initial concentration, colloid size and electrophoretic mobility were measured. The chemical composition of the water after the contact with the clay was analyzed. Size and charge of colloids were measured also upon progressive additions of Na⁺ or Ca²⁺ to check their stability and the concentration of monovalent or divalent cation needed to start coagulation process. The size of colloids was measured by Photon Correlation Spectrometry with a Malvern NanoS apparatus with He-Ne laser and at a measurement angle of 173°. Zeta potentials were determined with a Zetamaster Malvern system equipped with a Spectra-Physics 2mW He-Ne laser ($\lambda = 633 \text{ nm}$).

RESULTS AND DISCUSSION

Summary of main experimental data

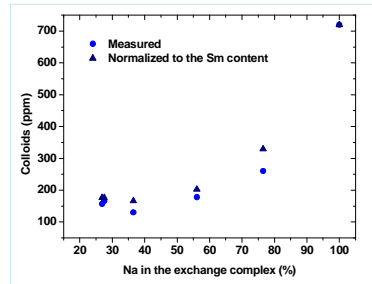
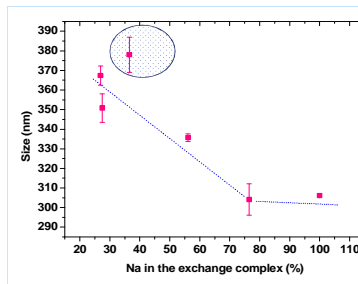
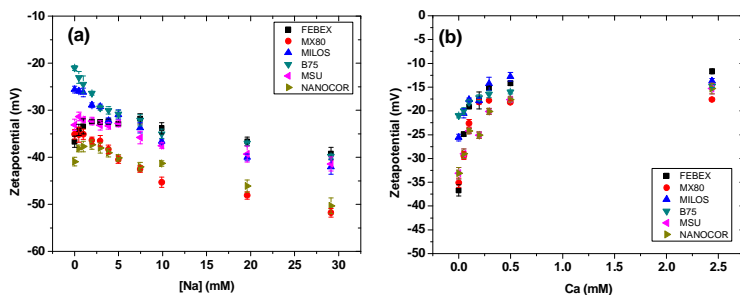
BENTONITE	Concentration of particles by gravimetry (mg/L)	Initial Size in DW	Init. Conductivity (μScm^{-1}) / and pH	Onset coagulation (Na, mM)	Onset coagulation (Ca, mM)
FEBEX	166±20	351±2	25.2 / 8.77	7-10	0.2-0.3
MX-80	178±10	336±2	28.5 / 8.75	5-7	0.2-0.3
IBECO/MILOS	157±10	367±2	56.8 / 9.47	2-3	0.1
B75	120±10	378±9	51.2 / 8.09	0.5-1	0.05
MSU	260±10	304±9	73.3 / 9.56	2-3	0.2
NANOCOR®	720±30	306±1	41.0 / 7.82	10-15	0.3

The quantity of colloids initially generated is summarized in Table 1; this provides a first indication of the “intrinsic” capability of the clays to disperse colloidal particles under favorable chemical conditions (DW).

For the selected bentonites, which are Na or Ca-Mg bentonites (with at least 20% of Na in the exchange complex), the generated colloids correlated quite well with the quantity of Na in the exchange complex, as can be observed in the Figure .

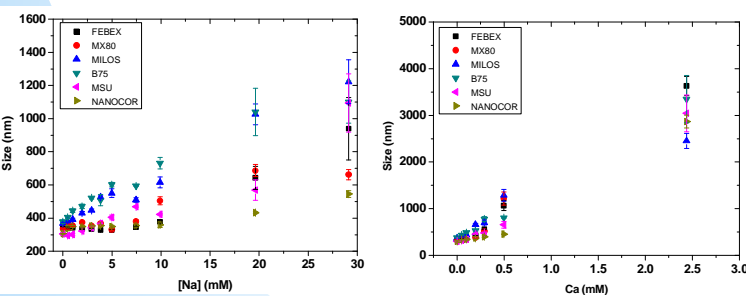
The initial colloid size was similar for all the bentonite considered (between 300 and 400 nm) and a good correlation with the Na content could be also found. The small deviation for B75 can be explained considering that most of its charge is located in the tetrahedral layer (72%).

Zetapotential measured at different concentrations of (a) Na or (b) Ca.



Na increase produced a slow decrease in the negative value of the zeta-potential. The behavior observed, upon the very first additions, is not exactly the same for all the clays and might be related to Na-Ca exchange processes. The addition of Ca, produced a pronounced and rapid decrease in the negative zeta-potential.

Colloid size measured at different concentrations of (a) Na or (b) Ca.



Na increase produced clay colloid aggregation, even if most of the clays present particles in the colloidal size range (<1 μm) even after the addition of 20-30 mM of Na. The onset of aggregation occurs at the lowest Na concentrations in the case of B75. Again, the location of the charge has a clear effect on particle aggregation. Adding Ca, the onset of coagulation is around 0.1 - 0.3 mM (more than one order of magnitude lower for Ca than Na is needed for aggregating the particles). For Ca concentration larger than 0.5 mM most of the clay particles have aggregated to give size larger than 1 μm . Again, the lowest Ca concentration for triggering coagulation is found for B75.

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CONCLUSIONS

The characteristics of the colloids, including their stability behavior can be related to intrinsic properties of the clay, specially the Na content in the exchange complex and the location of the surface charge. This work has been extended to more than ten additional clay for a more generalized study.