Analysis of the stability behaviour of colloids obtained from different smectite clays

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ABSTRACT

The analysis of the conditions affecting clay colloid stability is needed to assess the relevance of bentonite erosion processes and of bentonite colloids transport in the frame of a high-level radioactive waste repository.

Clay colloids ($< 1\,\mu m$ particle size) were extracted from several bentonites or smectite-rich clays with different physicochemical properties (i.e., smectite content, main exchanging cation, layer charge, charge distribution, etc.), by dispersing them in deionized water and collecting the supernatant after centrifuging. First, colloids were characterized to evaluate their initial size and electrophoretic mobility (surface potential). Then, their aggregation behaviour upon the addition of Na^+ or Ca^{2+} was studied, by analysing the evolution of both colloid size and electrophoretic mobility. The concentration of monovalent or divalent cation needed to start coagulation process (critical coagulation concentration, *CCC*) was estimated for each clay.

Despite the different initial clay colloids properties, their aggregation behaviour upon electrolyte additions was quite similar in all the cases. The aggregating power of Ca was observed to be much higher than that of Na, a Ca concentration of 0.3 mM being enough to aggregate any clay, compared to 1–20 mM of Na. The presence of Ca in solution is a critical and prevailing factor for clay particles aggregation, independently of other smectite bulk properties. The range of Na concentration needed to start the aggregation of different clay colloids is wider, but a relation between the measured CCC and other smectite bulk properties cannot be clearly established.

Nevertheless, the samples more resistant to aggregation were: the NANOCOR®, a Na-clay with the lowest percentage of tetrahedral charge, and the *as-received* and exchanged MX-80, which presents the lowest layer charge. The samples less resistant to aggregation were: the SAz-2, a Ca-clay with the highest layer charge and the lowest initial Na content, and the *as-received* and *exchanged* SBId-1, a beidellite, which presents a very high percentage of charge in tetrahedral position.

In stability tests, upon Na addition and consequent particle aggregation, an increase of the ζ-potential was observed, which is not in agreement with the double layer theory. Furthermore, the sample (Na)-SBId-1, which developed the highest surface potential, was the less resistant to aggregation. These results are a clear indication that the ζ-potential, alone, is not a very significant parameter to indicate or predict smectite colloid stability.

1. Introduction

Bentonites, which are foreseen as engineered barrier materials for high level radioactive waste (HLRW) repositories, are smectite-rich clays. Smectites have several interesting properties, especially related to cation and water retention or swelling (Pusch, 2006; Chapman and Hooper, 2012; Dohrmann et al., 2013; Sellin and Leupin, 2014; Kaufhold and Dohrmann, 2016).

The possible erosion of the bentonite barrier in a radioactive repository, leading to the generation of bentonite colloids, is a problem of concern (Sellin et al., 2013) because a significant bentonite mass loss might compromise the functionality of the barrier at the long-term and because the eroded particles, of colloidal size, might contribute to radionuclide (RN) migration (Möri et al., 2003; Schäfer et al., 2004; Missana et al., 2003, 2008; 2011; Albarran et al., 2011). Colloids, in fact, can move as fast as, or even faster than, groundwater if favourable conditions exist (Kretzschmar et al., 1999; Honeyman, 2001; Tang and Weisbrod, 2009; Schäfer et al., 2012).

The relevance of bentonite erosion and clay colloids transport is strictly related to the characteristics of the generated particles and to their stability under the chemical condition of the given scenario (Pusch, 1983; Missana et al., 2011; Albarran et al., 2014). Colloid size and surface charge control many important colloid-related processes as Brownian diffusion, sedimentation, migration, filtration, deposition on

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rock surfaces, as well as the interactions with radionuclides. On turn, all these properties depend on the chemistry of the medium in a complex way. Thus, phenomena controlling particle dispersion (and erosion) are also directly connected to the colloidal system stability.

Missana et al. (2018) analysed the intrinsic properties of colloids extracted from different bentonites (and smectite-rich clays), after suspending them in deionized water, to find out the main bulk properties favouring/hindering clay colloid detachment from the bulk (erosion) and affecting colloids behaviour. They analysed the effects of: smectite content, composition of the interlayer cations, layer charge, charge density and charge distribution between the tetrahedral (T) and octahedral (O) layer. They observed that the predominance of Na as interlayer cation favoured the formation of colloids with the smallest size and the highest electrophoretic mobility (EM), whereas the contrary occurred when Ca prevailed (i.e. larger colloids were formed with lower EM). The layer charge distribution was observed to play a role on the intrinsic clay colloid size which, independently on the main interlayer cation, increased when the tetrahedral charge increased. Additionally, a slight decrease of intrinsic EM was observed, as the tetrahedral charge increased.

The objective of the present study is to analyse if different intrinsic properties of smectite colloids, result in a different aggregation behaviour against the increase of electrolyte concentration.

Colloid aggregation occurs when, at the particle/liquid interface, the attractive forces overcome the repulsive double layer forces. An increase of ionic strength reduces the range of the surface potential, thus repulsive forces decrease, and particle attachment increases.

In the case of clay minerals, the ionic strength increase causes the formation of gels inhibiting particles release and restricting colloid stability (Luckam and Rossi, 1999; Missana et al., 2003). Smectites are 2:1 phyllosilicates where two tetrahedral sheets sandwich an octahedral sheet forming a TOT structure. These clay minerals possess a negative permanent charge arising from isomorphic substitutions in the phyllosilicate layers, which is compensated by the presence of cations in the interlayer. Thus, clay colloids possess a constant charge (Luckam and Rossi, 1999). Additionally, they present a small variable amphoteric charge coming from the functional groups (Si–OH, silanols, and Al–OH, aluminols) at the edges of the clay particles, where Si–O–Si and Al–O–Al bonds are broken (Güven, 1988; Tombacz and Szkeres, 2004). Electrostatic interactions between TOT layers, giving rise to particle aggregation, can be face to face, FF, edge to edge, EE, or edge to face, EF (van Olphen, 1977). Even if EE or EF interactions cannot be completely ruled out, under the conditions of the experiments (pH neutral to alkaline), the predominance of FF interactions is expected.

The ionic strength has been reported to be a relevant parameter in relation to bentonite erosion: salinity higher than 10–20 mM (in Na) was found to inhibit almost completely bentonite erosion in different clays and under different experimental configurations (Schatz et al., 2016; Missana, 2016). However, the difference in the response to ionic strength increase, in smectites with different properties, has not been analysed in detail yet.

In this study, the aggregation behaviour of colloid extracted from different clays upon the addition of different concentrations of Na^+ or Ca^{2+} was studied, analysing both colloid size and EM (or ζ-potential) evolution. The concentration of monovalent or divalent cation needed to start coagulation process was measured to experimentally determine the ion critical coagulation concentration (CCC) for each clay.

The stability behaviour observed for the different clay colloids will be discussed based on the clay bulk and intrinsic colloid properties.

2. Materials and methods

2.1. Clays

Different clays were selected for this study, trying to cover a comprehensive range of physicochemical properties. Most of them are

bentonites which have been already studied in the frame of international projects related to HLRW. In addition, three commercial dioctahedral smectites were obtained from the Clay Minerals Society Source Clays Repository (SBId-1, NAu-1, SAz-2) and another one was supplied by NANOCOR® (China). They are summarised below:

- FEBEX bentonite, mined in Cortijo de Archidona, Almería, Spain (Huertas et al., 2000; Fernández et al., 2004).
- Bentonite from Milos Island in the Aegean Sea, Greece (Koch, 2008). The Milos bentonite is mined by Silver & Baryte Mining Company S.A, and its commercial name is IBECO (the sample under study is IBECO RWC 16).
- Wyoming MX-80 bentonite from USA produced by Am. Coll. Co (Müller-Vonmoss and Kahr, 1983).
- Two Czech bentonites extracted from the Rokle deposit, in the Kadan basin, c. 100 km WNW of Prague. The bentonite from this deposit is highly variable in colour, ranging from olive-grey to yellow/red due to the admixture of secondary iron and manganese oxides. The clay referred as to Rokle-S65 (Sabenil) is a fully Na-activated commercial clay (Konta, 1986); the Rokle-B75 is a partially Na activated clay.
- Russian bentonite from the Khakassia deposit (Sabodina et al., 2006). This clay is named MSU (the name given by the Moscow State University).

The four commercial dioctahedral smectites are:

- NANOCOR® (China), that is a Na-exchanged and purified *montmorillonite* (http://www.nanocor.com/). It has been used as reference material in the recent European BELBAR project (http://www.skb.se/belbar/).
- SBId-1 (Clay Mineral Society): it is a *beidellite* from Idaho, USA (Post et al., 1997).
- NAu-1 (Clay Mineral Society): it is a *nontronite i.e* a ferruginous (4.50 mmol Fe g^{-1}) smectite coming from the Uley Graphite Mine in South Australia (Keeling et al., 2000).
- SAz-2 (Clay Mineral Society): it is also known as "*Cheto*" clay (Jaynes and Bigham, 1987) and it is mined in the state of Arizona, USA.

The samples were all used "*as-received*" and some of them were also exchanged with Na or Ca. To exchange the clays, they were washed three times with the respective Na/Ca electrolyte (1 M $NaClO_4$ or Ca $(ClO_4)_2$) and then washed with deionized water (DW) and DW/ethanol until the electrical conductivity of the suspension was lower than 100 μS cm^{-1}. Afterwards the exchanged clays were dried in the oven and finally powdered in an agate mortar.

A complete geochemical and mineralogical characterization of the *as-received* clays was carried out by different techniques to evaluate major and minor minerals, phyllosilicate and smectite content, cation exchange capacity, major cations, water content, pore water chemistry, BET and total surface area, charge distribution and cell formula. Same techniques and methodologies were applied for all the clays. All the details of this work can be found elsewhere (Fernandez et al., 2018). A summary of the parameters of interest for this study is presented in Table 1.

2.2. Clay colloids preparation

Clay colloids (size < 1 μm) were extracted from the different *as-received* or exchanged clays by dispersing them (1 g L^{-1}) in DW and collecting the supernatant upon centrifuging at approximately 3000 rpm (equivalent to 700*g*, where *g* is the relative centrifuge force), during 10 min. DW was used to maximize clay colloid dispersion and the solid to liquid ratio was selected to minimise the possible chemical effects produced by soluble salts, or eventual clay mineral dissolution,

Table 1
Main physicochemical characteristics of the clays used in this study.

Clay	Sm content (wt. %)	Na at exchange sites (%)	Ca + Mg at exchange sites (%)	Layer charge (e/h.u.c)	Charge density (C/m²)	Tetrahedral Charge (e/h.u.c, %)	Octahedral Charge (e/h.u.c)
FEBEX	94	28.0	66.4	0.38	0.13	0.06 (16)	0.32
IBECO	88	26.3	69.0	0.33	0.11	0.04 (12)	0.29
MX-80	89	68.3	26.3	0.28	0.10	0.08 (28)	0.20
Rokle-B75	78	55.7	34.6	0.40	0.14	0.29 (73)	0.11
Rokle-S65	78	76.9	16.7	0.37	0.13	0.26 (70)	0.11
MSU	79	90.2	4.46	0.35	0.12	0.14 (40)	0.21
NANOCOR*	98	93.5	2.51	0.38	0.13	0.04 (11)	0.34
SBId-1 (Beidellite)	78	0.7	92.0	0.32	0.11	0.26 (81)	0.06
NAu-1 (Nontronite)	90	3.8	91.3	0.37	0.12	0.32 (86)	0.05
SAz-2 – Cheto	98	0.4	92.3	0.50	0.17	0.00 (0)	0.50

on the solution chemistry.

The water in equilibrium with the colloidal phase, after being filtered by 0.2 μm with a Millipore membrane, was analysed to determine the presence of different types of ions leached from the clays. Measurements of pH (± 0.1) were made using a Mettler Toledo (S220) pH-meter with a solid polymeric electrode (Xerolyt) or a Crison pH-ion meter (GLP225) with a combined glass pH electrode (Metrohm). Electrodes calibration was made with buffer solutions at pH 2, 4, 7 and 10. Conductivity measurements were carried out with a Crison EC Meter Basic 30⁺.

2.3. Colloid size measurements

Clay colloids size (intensity-averaged particle diameter) was measured by dynamic light scattering with a Malvern NanoS apparatus with He-Ne laser and at a measurement angle of 173°. The *intrinsic* colloid size is referred to the measurement made in the initial colloid suspension, in DW, where the possible effects of water chemistry on particle aggregation are minimized.

To evaluate colloid stability as a function of the ionic strength, and to determine the concentration of electrolyte needed to start aggregating colloids, the size was measured after additions of different aliquots of Na⁺ (up to 30 mM) or Ca²⁺ (up to 2.5 mM), as NaClO₄ or Ca(ClO₄)₂, in 20 mL of the initial suspension. Measurements were carried out approximately 24 h after the electrolyte addition.

The *onset of coagulation* was taken as the colloid size incremented about a 30% in respect to the initial one. The concentration of monovalent or divalent cation needed to start coagulation process (critical coagulation concentration, CCC) was, thus, experimentally estimated for each clay, at the initial pH of the suspension (Table 2). The value of Na⁺ concentration needed to bring the particle size out of the colloidal range (> 1 μm) was also recorded (Table 2).

2.4. Colloid surface charge: electrophoretic mobility measurements

In parallel to colloid size measurements, the *intrinsic* colloid electrophoretic mobility (EM) and its evolution, upon the addition of different quantities of Na⁺ or Ca²⁺, was measured by laser Doppler electrophoresis with a Zetamaster Malvern system equipped with a 2 mW He-Ne laser (λ = 633 nm).

According to the Gouy-Chapman theory of the electrical double layer (EDL), which is widely used to describe colloid behaviour, the relationship between the surface charge density, σ, and the surface potential, ψ, (for a symmetric electrolyte) is given by:

$$\sigma = \sqrt{8n\varepsilon kT} \sinh\left(\frac{ze\psi}{2kT}\right) \tag{1}$$

Where n is the bulk concentration of ions of valence z, ε the permittivity, k the Boltzmann constant, T the absolute temperature and e the electron charge.

Table 2
Properties of the initial colloid suspensions. The prefix (Na)- or (Ca)- indicates that the clay is homoionised in the specified ion.

Sample	pH	Cond (μS·cm⁻¹)	I (M) ·1·10⁻⁴	Size (nm)	Electrophoretic Mobility (μm·s⁻¹)/(V·cm⁻¹)
FEBEX	8.8	25.2	2.74	349 ± 1	−2.18 ± 0.07
IBECO	8.9	44.8	3.48	367 ± 5	−1.80 ± 0.05
MX-80	9.4	56.8	5.11	336 ± 2	−2.57 ± 0.08
Rokle-B75	7.2	21.3	2.02	378 ± 9	−1.50 ± 0.04
Rokle-S65	9.1	10.9	2.85	415 ± 5	−2.00 ± 0.06
MSU	8.7	28.5	5.17	304 ± 8	−2.37 ± 0.07
NANOCOR*	7.8	40.9	10.60	250 ± 10	−2.96 ± 0.09
SBId-1 (Beidellite)	8.4	14.1	0.58	700 ± 100	−2.60 ± 0.15
NAu-1 (Nontronite)	7.6	29.7	0.96	783 ± 62	−2.30 ± 0.11
SAz-2 – Cheto	8.5	14.0	0.99	550 ± 100	−1.47 ± 0.09
(Ca)-FEBEX	6.7	14.2	2.25	600 ± 15	−1.30 ± 0.04
(Na)-FEBEX	7.0	11.6	2.13	260 ± 10	−2.50 ± 0.04
(Ca)-MX-80	9.2	14.2	1.82	523 ± 25	−1.18 ± 0.03
(Na)-MX-80	8.8	12.2	(nd)	249 ± 10	−2.70 ± 0.08
(Na)-SBId-1	8.4	14.1	1.65	539 ± 9	−2.71 ± 0.08

The ζ-potential is the potential produced by the double layer near the electrolyte/particle interface at the location of the "*slipping plane*", which limits the layer of fluid adhered to the particle moving with it. Thus, the ζ-potential is not exactly equal to the surface potential generated by the surface charge of the particles, but it is often the only possible mean to characterize surface charge at least in terms of sign and magnitude (Delgado et al., 2007). Therefore, ζ-potential is often used in predictive models of colloid stability in substitution of the actual electrical surface potential and for this reason this magnitude is considered of special importance.

The ζ-potential can be estimated by electrophoretic techniques, by measuring the velocity and direction of charged particles under a given electric field. i.e. by evaluating their electrophoretic mobility, EM, which is the velocity of the particles divided by the magnitude of the applied electric field (μm·s⁻¹)/(V·cm⁻¹).

The mobility is converted to ζ-potential considering the properties of the fluid (dielectric constant, ε, and viscosity, η) by different theoretical approximations (Delgado et al., 2007). The Henry expression relates the EM to the ζ-potential according to the following formula:

$$EM = \frac{2\varepsilon\zeta f(\kappa a)}{3\eta} \tag{2}$$

In Equation (2), f(κa) is the Henry function, which varies from 1 to 1.5.

The best-known theory to calculate ζ-potential from electrophoretic mobility data is the Smoluchowski approximation. In that case, f(κa) = 1.5 and Eq. (2) is equivalent to the Helmholtz-Smoluchowski
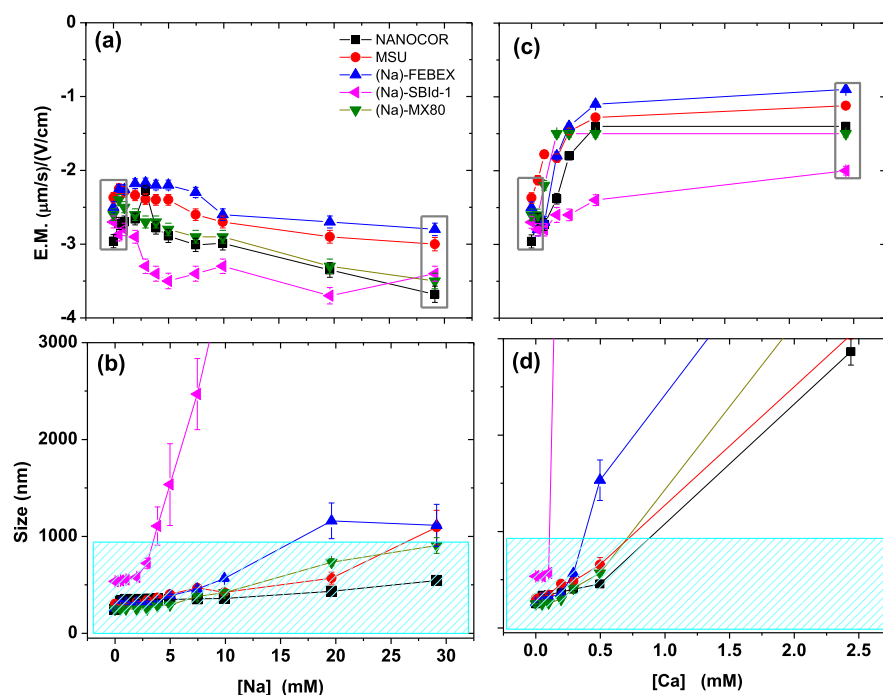
Fig. 1. Evolution of: (a, c) electrophoretic mobility and (b, d) colloid size as a function of the added Na (left) or Ca (right) for Na-clays. (<) NANOCOR; (=) MSU; (▲) (Na)-FEBEX; (◀) (Na) SBiD-1; (▼) (Na)-MX-80.

equation (Delgado et al., 2007). The Smoluchowski approximation is valid only when the Debye length $(1/\kappa)$ is much smaller than the particle radius (a), therefore it is adequate for particles larger than about $0.2\,\mu m$ and dispersed in electrolytes containing more than $10^{-3}\,M$ concentration of salts.

This condition can be expressed as: $\kappa{\cdot}a \gg 1$ where

$$\kappa = \sqrt{\frac{\sum_i e^2 z_i^2 n_i}{\varepsilon kT}} \tag{3}$$

In Equation (3), e is the charge of the electron, z_i is the valence of the ion i present in the electrolyte, k is the Boltzmann constant, T the absolute temperature, n_i the number concentration of the ion i, and ε $(\varepsilon_r{\cdot}\varepsilon_0)$ the absolute permittivity.

In other cases (i.e., when $\kappa{\cdot}a$ is not $\gg 1$), this approximation must be substituted by other theories.

As the initial salinity of suspensions was very low, because clays were dispersed in DW, the Smoluchowski approximation could not be always used to determine the *intrinsic* ζ-potential, therefore data were expressed only in terms of EM. A comparison of ζ-potential data for all the clays will be done with the measurements carried out upon the addition of 10 mM of Na, which is a value near to the reported threshold to stop clay erosion (Schatz et al., 2016). Upon the addition of this quantity of Na, the calculated $\kappa{\cdot}a$ values are around 60–100, thus the Smoluchowski approximation can be applied.

3. Results and discussion

3.1. Characteristic of the initial clay suspensions

The characteristics of the different initial colloid suspensions are reported in Table 2. Values of pH varied from 7 to 9.5 and the electrical conductivity from 10 to $90\,\mu S\,cm^{-1}$ approximately. This is a first indication that a different quantity of ion leached from the clays can be present in solution, due to the different salt inventory and to some clay dissolution, as clay hydrolysis in deionized water cannot be ruled out. However, the initial ionic strength, calculated on the bases of the performed chemical analyses, indicated in all the cases very low salinity, with a maximum for NANOCOR® (around $1{\cdot}10^{-3}\,M$) and minimum

$(6{\cdot}10^{-5}\,M)$ for the beidellite, SBiD-1.

Aggregation effects due to these low ionic strengths should be very limited, thus the initial measured size can be considered as the *intrinsic* clay colloid size. The intrinsic size and EM are also reported in Table 2.

As can be seen in Table 2, the intrinsic mean size of smectite colloids is quite variable: from approximately 250 nm (NANOCOR® or (Na)-MX-80) to almost 800 nm (*nontronite*, NAu-1). Instead, the intrinsic EM values (in $(\mu m{\cdot}s^{-1})/(V{\cdot}cm^{-1})$) measured for the analysed smectites, were not extremely different, with a minimum of -0.75 for the (Ca)-IBECO to a maximum of -2.96 for the NANOCOR®. The EM is always negative, reflecting the permanent negative charge of 2:1 clays (Sondi et al., 1996; Luckam and Rossi, 1999), thus *decrease and increase* in EM will be referred to its absolute values.

As mentioned in the introduction, Missana et al. (2018) showed that colloids intrinsic size and EM could be related to the physicochemical properties of the bulk clay. The question is now to verify to what extent these properties may affect the overall stability behaviour of clay colloids against an increase of ionic strength.

3.2. Variation of colloid size and EM as a function of the electrolyte concentration

To facilitate the comparison of all the results, the clays were divided in three groups: Na-clays; Ca-clays and (Na,Ca)-mixed clays. Na-clays are those with Na > 80% and Ca + Mg < 10% as interlayer cations; Ca-type those with Ca + Mg > 70% and Na < 10%; (Na,Ca)-mixed clays all the others with intermediate values for Ca + Mg and Na.

The results of the stability tests for Na-clays, (Na,Ca)-mixed clays and Ca-clays are summarised in Fig. 1 to Fig. 3, respectively.

3.2.1. Na-clays

Fig. 1 shows the variation of the EM (Fig. 1a and c) and colloid size (Fig. 1b and d) for Na-clay colloids upon the addition of NaClO$_4$ (Fig. 1a and b) and Ca(ClO$_4$)$_2$ (Fig. 1c and d).

Upon the addition of both Na or Ca electrolytes, the trend of EM variation is qualitatively similar for all the Na-clays, within approximately 1 unit of $(\mu m{\cdot}s^{-1})/(V{\cdot}cm^{-1})$.

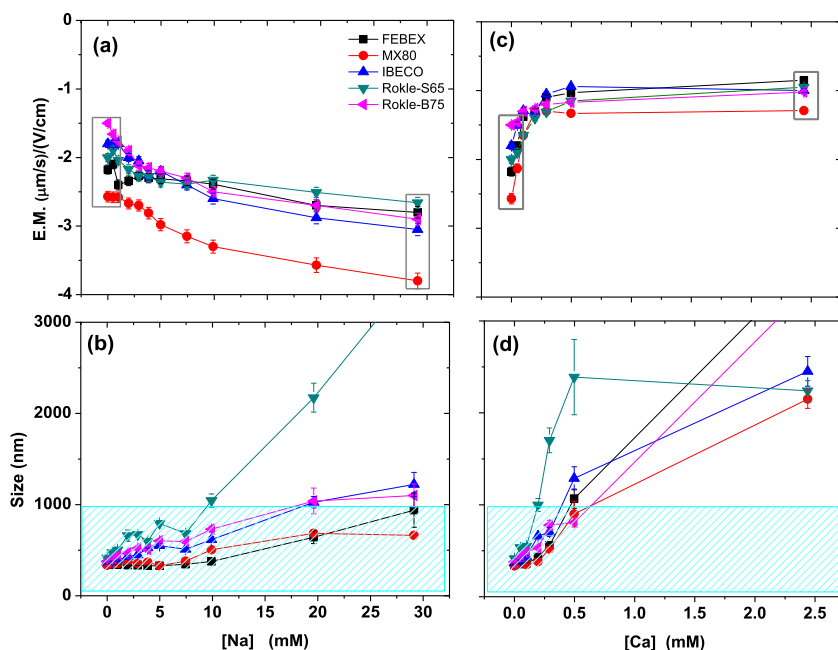However, when Na is added the EM shows a small progressive

Fig. 2. Evolution of: (a, c) electrophoretic mobility and (b,d) colloid size as a function of the added Na (left) or Ca (right) for (Na,Ca)-mixed clays. (◄) FEBEX; (■) MX-80; (▲) IBECO; (◄) Rokle-B75; (▼) Rokle-S65.

increase (Fig. 1a), whereas when Ca is added (Fig. 1c) the opposite trend is seen, as the EM tends to decrease reaching rapidly a *plateau*.

The intrinsic EM values of Na-clays ranged approximately between −2 and −3 (μm·s^{-1})/(V·cm^{-1}) and, after the addition of 30 mM of Na, they varied from −2.5 to −3.8 (μm·s^{-1})/(V·cm^{-1}); instead, upon the addition of 2.5 mM of Ca, they varied between −1 and −2 (μm·s^{-1})/(V·cm^{-1}).

Even a different trend of EM was observed upon Na (Fig. 1b) or Ca (Fig. 1d) addition, in both cases particles aggregation was clearly observed. The range of particle size smaller than 1 μm (colloidal) is indicated in the figures as a light blue area.

After the addition of 10 mM of Na, almost all the Na-clay colloids

still have a size lower than 1 μm, and some clay would need the addition of more than 30 mM of Na to form aggregates with a size larger than 1 μm. On the other hand, all the Na-clays are aggregated with sizes out of the colloidal range, with the addition of 1 mM of Ca. This clearly indicates that the aggregating power of Ca is much stronger than that of Na.

Particle aggregation is expected when the ionic strength increases, because considering the EDL theory (e.g., van Olphen, 1977), the increase of salinity provokes the shrinking/diminution of the electrical potential around the particles, thus less resistance to aggregation upon collisions.

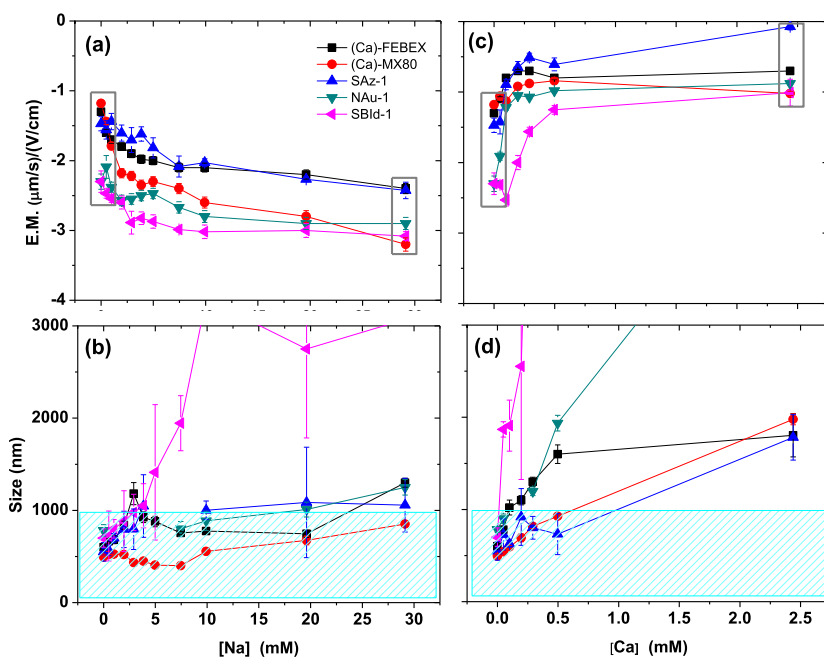Calcium is a divalent ion which, in principle, favours a better

Fig. 3. Evolution of: (a, c) electrophoretic mobility and (b,d) colloid size as a function of the added Na (left) or Ca (right) for Ca-clays. . (◄) (Ca)-FEBEX; (■) (Ca)-MX80; (▲) SAz-2; (◄) SBiD-1; (▼) NAu-1.

neutralization of the clay layer charge, which can explain why the EM decreases fast in the presence of Ca in solution. The fact that upon Na addition, the surface potential is increasing (Fig. 1a) is not in agreement with the Gouy-Chapman theory and the conventional description of the EDL. Considering Eq. (1), if the charge density is a constant (as expected in the case of 2:1 clays), the surface potential should decrease if the electrolyte concentration increases, as the double layer is shrinking. Slight increase or no dependence of clay mobility (or ζ-potential) on Na concentration in solution (from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$ M) was also observed in previous studies (Horikawa et al., 1988; Lebron and Suarez (1992); Missana and Adell (2000)). Horikawa et al. (1988) suggested that clays must have almost constant surface potential within a large range of Na concentration and must be considered as surfaces of constant potential rather than constant charge, arguing the Gouy-Chapman theory. Some authors explained this supposed anomaly, considering the existence of a charge spillover caused by layer compression (FF) i.e. a sort of re-arrangement of the electrical field around the edges of clay particles. As the edges (neutral or positively charged) are screened, the net negative charge increases. This spillover occurs with Na because the double layer produced by Na ions is not as compact as that produced by divalent ions (Lebron and Suarez, 1992).

In any case, even if the EM increases, the fact that the double layer is less repulsive increasing the Na content is demonstrated by the evident aggregation of the particles. Thus, EDL theory may not be directly applicable to explain the charge behaviour of clay particles, and other mechanisms than those described by Gouy Chapman theory, should be accounted for. Furthermore, the sample that aggregates faster upon both Ca or Na addition is the Na-exchanged beidellite, (Na)-SBId-1 which develops the highest surface potential and form viscous suspensions. This result is a further indication that the ζ-potential alone, might not be a very significant parameter to estimate the stability of smectite colloids.

3.2.2. (Na, Ca)-mixed and Ca-clay colloids

Figs. 2 and 3 show the variation of the EM (a, c) and colloid size (b, d) for Na-clay colloids upon the addition of NaClO$_4$ (a, b) and Ca(ClO$_4$)$_2$ (c, d), for mixed and Ca-clays respectively.

The results obtained for (Na,Ca)-mixed and Ca-clays are qualitatively similar to those already discussed for Na-clays. The intrinsic EM values of (Na,Ca)-mixed and Ca-clays range approximately from −1.5 to −2.5 and −1.0 to −2.5 (μm·s^{-1})/(V·cm^{-1}) respectively. Upon Na addition (30 mM), EM increases reaching values between −2.5 and −4 (μm·s^{-1})/(V·cm^{-1}), in the case of (Na, Ca)-mixed clays, and between −2 and −3 (μm·s^{-1})/(V·cm^{-1}), in the case of Ca-clays. Instead, upon Ca addition (2.5 mM), EM values decrease reaching values between −1 and −1.5 (μm·s^{-1})/(V·cm^{-1}), in the case of (Na,Ca)-mixed clays, and between −1 and 0 (μm·s^{-1})/(V·cm^{-1}), in the case of Ca-clays.

Again, despite the increase/decrease of the initial EM, observed upon Na or Ca additions, the particle size always increases, indicating that the surface potential is less repulsive.

Table 3 shows the summary of the results obtained in all the stability tests and in particular: a) the concentration of Na and Ca needed to start the coagulation process (which produces the aggregation to a size a 30% bigger than the initial one), that will be assumed as the CCC of the clay; b) the concentration of Na, needed to aggregate the particles to a size bigger than 1 μm; c) the EM, d) ζ-potential and d) clay colloid size upon the addition of 10 mM of Na; e) the size of the particles after the addition of 0.2 mM Ca.

The general behaviour upon the electrolytes addition is similar for all clay types. The CCC measured here are within the range of those reported by other authors (Liu et al., 2009). The addition of either Na or Ca induces an increase of the colloid size: the concentration of Na needed to onset colloid aggregation varied from 1-2 mM to 10–20 mM, whereas the Ca concentration was much smaller (from 0.05 to 0.3 mM). As observed in the tests, the addition of Ca in solution is a critical and prevailing factor for clay particles aggregation, independently on the

bulk properties of the smectite.

The Schulze-Hardy rule assumes that the CCC$_{(i)}$ of an ion (i) depends on the sixth power of its valence (CCC ~1/z$_i^6$), thus the theoretical ratio for CCC$_{(Na)}$/CCC$_{(Ca)}$ should be 64; from the data obtained in present work, it can be deduced that this ratio is not the same for all the smectites but a clear relation between the measured CCC and other smectite bulk properties cannot be established. The concentration of Na needed to aggregate clay colloids to a size bigger than 1 μm, is quite spread (from 3 to 4 mM to > 30 mM but, neither in this case, a clear relation with other clay bulk properties could be found.

Some possible reasons make difficult to establish these relations. First of all, it has to be considered that the initial colloid concentration is not the same in all the samples because Na-clays for example, form much more colloids than Ca-clays (Missana et al., 2018). Furthermore, part of the added Na, is adsorbed in the clay by ionic exchange and the ion selectivity is not necessarily the same for all the clays. Finally, Shainberg and Otoh (1968) reported that when Na$^+$ and Ca^{2+} are simultaneously present, they are not evenly distributed in the clay particles but that Na$^+$ ions are preferentially located on surface and Ca^{2+} at the clay interlayer *(demixing process)*. The (re)distribution of ions occurs basically by a diffusion process and its kinetic may also vary from one clay to another.

In general terms, however, some details related to the intrinsic colloid properties that may have some effects on the overall stability can be still pointed out. The samples more resistant to aggregation are the NANOCOR® and *as-received* and exchanged MX-80; the less resistant ones are the SAz-2 and the SBId-1 (*as-received* and exchanged). The MX-80 has the lowest layer charge and the SAz-2 the highest. NANOCOR® has a very high (initial) Na content and low tetrahedral charge; SBId-1 has high tetrahedral charge. A combination of various factors as: high layer charge, high tetrahedral charge and high Ca content as exchange cation, should in principle favour the aggregation process even if, in stability tests where external electrolyte is added, ionic exchange processes modifying system equilibrium, cannot be obviated.

In the end, a comparison the size and ζ-potential, of the clay colloids, after the addition of 10 mM of NaClO$_4$, was made. Fig. 4 shows the ζ-potential (Fig. 4a) and size (Fig. 4b) of the clay colloids upon the addition of 10 mM of Na, as a function of the initial quantity of Na as interlayer cation.

As already mentioned, after Na addition, exchange processes are expected to occur modifying the exchange complex and the supernatant composition.

The values of ζ-potentials of the "aggregated" colloids are all constrained in a range between −30 and −45 mV and, in general terms, they seem still having a relation with the (initial) quantity of Na in the interlayer, because, Na-clays present the highest surface potentials and Ca-clays the lowest, as occurred in the case of intrinsic particles (Missana et al., 2018). Even relatively small differences in ζ-potentials values exist, the size of aggregated particles is quite scattered, with values from approximately 400 to 3700 nm, and it does not maintain a relation with the initial Na content. In particular, the largest particles correspond to the beidellite, SBdI-1, both in the as-received and Na-exchanged form. This clay, which has high tetrahedral charge, forms large particles and quite dense gels even in deionized water as reported by Missana et al. (2018), who suggested that this sample may form EF aggregates, forming large structures with a random distribution of platelets. It is interesting noticing that this clay shows the highest ζ-potential, thus this parameter alone seems not to be predictive of clay mineral stability.

The predominance of tetrahedral charge, which produced a clear increase of the intrinsic size of the particles (Missana et al., 2018), still have a certain effect on the size of the aggregates especially in the case of Na-clays and (Na,Ca)-mixed clays (Table 3).

Table 3
Summary of the stability tests performed on different clay colloids.

CLAY	Onset Coag. (Na) (mM)	Onset. (Ca) (mM)	Size > 1 μm (Na, mM)	EM 10 mM Na (mV)	Zeta at 10 mM Na (mV)	Size at 10 mM Na (nm)	Size at 0.2 mM Ca (nm)
FEBEX	10–20	0.2–0.3	20–30	−2.4 ± 0.1	−33.8 ± 1.2	377 ± 6	432 ± 5
IBECO	3–4	0.1–0.2	10–20	−2.6 ± 0.1	−36.6 ± 0.5	615 ± 33	660 ± 24
MSU	4–5	0.1–0.2	20–30	−2.7 ± 0.1	−37.5 ± 0.6	423 ± 4	458 ± 11
MX-80	7.5–10	0.2–0.3	> 30	−3.3 ± 0.1	−42.2 ± 2.0	504 ± 24	382 ± 12
NANOCOR*	10–20	0.3–0.5	> 30	−3.0 ± 0.1	−41.3 ± 0.6	360 ± 16	371 ± 25
NAu-1 (Nontronite)	7.5–10	0.2–0.3	10–20	−2.8 ± 0.1	−37.4 ± 0.9	886 ± 105	1000 ± 100
Rokle-B75	3–4	0.1–0.2	10–20	−2.5 ± 0.1	−35.0 ± 0.5	731 ± 36	553 ± 13
Rokle-S65	1–2	0.1–0.2	5–7	−2.3 ± 0.1	−31.7 ± 0.7	1045 ± 73	998 ± 72
SAz-2 – Cheto	1–2	0.1–0.2	4–5	−2.0 ± 0.1	−29.5 ± 0.8	1001 ± 100	918 ± 308
SBId-1 (Beidellite)	2–3	< 0.05	3–4	−3.0 ± 0.1	−44.4 ± 1.3	3290 ± 200	2553 ± 500
(Ca)-FEBEX	2–3	0.05–0.1	3–4	−2.1 ± 0.1	−30.2 ± 0.8	775 ± 26	1100 ± 50
(Na)-FEBEX	4–5	0.2–03	10–20	−2.6 ± 0.1	−37.2 ± 1.0	566 ± 31	353 ± 10
(Ca)-MX-80	10–20	0.1–0.2	> 30	−2.6 ± 0.1	−36.4 ± 0.6	556 ± 36	692 ± 42
(Na)-MX-80	5–7.5	0.2–03	> 30	−2.9 ± 0.1	−41.5 ± 1.0	419 ± 9	298 ± 7
(Na)-SBId-1	2–3	0.1–0.2	3–4	−3.3 ± 0.1	−47.1 ± 2.8	3683 ± 410	6482 ± 157
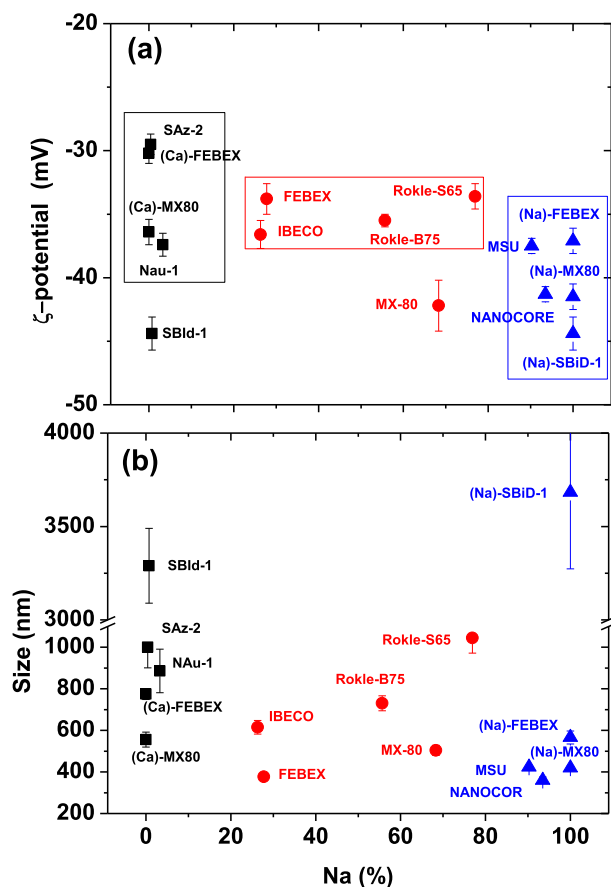
Fig. 4. a) ζ-potential and b) colloid size of the different samples upon the addition of 10 mM Na, as a function of the initial Na content as interlayer cation. (▲) Na-clays; (●) (Na, Ca)-mixed clays and (■) Ca-clays.

4. Conclusions

The aggregation behaviour of colloids extracted from several smectite-rich clays with different physicochemical properties was analysed upon the addition of Na$^+$ or Ca^{2+} and the concentration of monovalent or divalent cation needed to start coagulation process (*CCC*) for each clay was experimentally determined.

Even though the initial properties of clay colloids were different, their overall aggregation behaviour was similar in all the cases. The CCC of Ca, CCC$_{Ca}$, varied approximately between 0.05 mM and 0.3 mM, the CCC of Na, CCC$_{Na}$, from 1 to 20 mM. This is in qualitative agreement with the Schultze-Hardly rule, even the theoretical ratio (CCC$_{Na}$/CCC$_{Ca}$) should be 64, and it was variable from clay to clay.

Calcium in solution is a predominant element to trigger particles aggregation, independently of other smectite bulk properties. Sodium in solution starts colloid aggregation in a broader range of concentration, but a relation between the measured CCC$_{Na}$ and initial clay properties could not be established. Nevertheless, a combination of various factors as: high layer charge, high tetrahedral charge and high Ca content as interlayer favours the aggregation process. Ionic exchange processes and the kinetics of redistribution of ions at the clay particle surface/interlayers, that can take place after electrolyte addition, may affect the overall stability behaviour and cannot be ruled out.

The ζ-potential is not a very significant parameter to predict smectite colloid stability. The surface potential was observed to slightly decrease upon Na addition to the clay suspension, a fact which cannot be explained by the Gouy-Chapman theory, considering that 2:1 clay minerals present constant charge density. Thus, the double layer theory may not be directly applicable to explain the charge and stability behaviour of smectite particles.

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