



Colloidal properties of different smectite clays: Significance for the bentonite barrier erosion and radionuclide transport in radioactive waste repositories

Tiziana Missana*, Ursula Alonso, Ana María Fernández, Miguel García-Gutiérrez

CIEMAT, Department of Environment, Avenida Complutense 40, 28040, Madrid, Spain

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ABSTRACT

Compacted bentonite is envisaged as engineered barrier in high-level radioactive waste (HLRW) repositories and, to assess its functionality at a long term, many clay properties must be investigated. Bentonite erosion poses a potential problem, because a significant mass loss would jeopardize the performance of the barrier; in addition clay colloids generated from the eroded material might play a role on radionuclide transport.

In this study, the intrinsic characteristics of colloids obtained from different smectitic clays (mass, size and surface charge) were analysed, focusing on their relation with the main physicochemical properties of the bulk clays: the smectite content, the composition of interlayer cations, the total layer charge and its distribution between the tetrahedral and octahedral layer.

Results demonstrated that the predominance of Na as interlayer cation highly favours colloid detachment and the formation of colloids with the smallest size and the highest electrophoretic mobilities; the contrary occurs when Ca prevails (less detachment, larger colloids and lower mobilities). Besides, apart from the Na/Ca content, also the layer charge and charge distribution were shown to affect the intrinsic colloidal properties. For example, the increase of tetrahedral charge (τ) provokes stronger interactions between the TOT smectite layers, because cations (especially divalent) can be better bound to the clay surface. A τ increase causes the formation of larger aggregates with less probability of detachment. However, if the main exchange ion is Na, which strongly favours clay dispersion, high τ gives rise to an increased mass loss as, in fact, the released particles are bigger.

The results were discussed in a generalised form, concluding on the potential erodibility of different smectites and the implications of this erosion on radionuclide migration in a HLRW repository.

1. Introduction

Smectite clays are of great scientific interest for their many industrial and environmental fields of application as: nanocomposite, drilling fluids, adsorbents, paints, confinement of hazardous waste (Meunier, 2005; Mukherjee, 2013). Thus, their physicochemical attributes have been studied in detail since the decade of '70, mainly to establish their adequacy for different uses. In particular, bentonites (clay materials with high smectite content) have been largely investigated for their potential use as barrier and buffer materials in high level radioactive waste (HLRW) repositories as they present, amongst other interesting properties, good swelling capacity, low hydraulic conductivity, high sorption capability and ability to seal cracks (Pusch, 2006; Chapman and Hooper, 2012; Dohrmann et al., 2013; Sellin and Leupin, 2014; Kaufhold and Dohrmann, 2016).

At present, the possible “erosion” of the bentonite barrier of HLRW repositories, 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 if favourable environmental conditions exist (Missana et al., 2003, 2011; Moreno et al., 2011; Kaufhold and Dohrmann, 2016).

The term “bentonite erosion” it is used in this context to indicate the release of particulate material from the surface of the clay barrier, independently on the causes producing it. It does not refer only to the detachment caused by mechanical forces (i.e. water flow), but also to chemical processes, that favour repulsion between clay platelets and consequent dispersion in the aqueous phase.

Robust models are needed to calculate the extent of bentonite

* Corresponding author.

E-mail address: tiziana.missana@ciemat.es (T. Missana).

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eroded mass and to predict colloid-mediated RN migration under different environmental conditions and new experimental data are required to develop them.

In a repository, after its hydration and swelling, the bentonite will penetrate into the rock fissures. When groundwater touches the clay, the removal of particles can be originated either by diffusion or by mechanical forces. Clay erosion could be promoted by mechanical stresses produced by the water flowing at its surface, which would also facilitate the dragging of particles and aggregates. This mechanical erosion is expected to depend on water velocity and fracture characteristics (Pusch, 1999; Birgersson et al., 2009; Missana et al., 2011; Svoboda, 2013).

Nevertheless, the chemistry of the system is extremely important on erosion processes and might be a dominant factor even in the presence of a water flow, as it has been reported elsewhere (Missana et al., 2003, 2011; Albarran et al., 2014). The probability of clay erosion increases, in fact, with its capacity to spontaneously disperse in water (Pusch, 1983). Thus, the release of particles will be governed by those factors which cause dispersion or flocculation, that are dependent on the chemistry of the system and the colloidal properties of the clay.

Moreover, the physicochemical characteristics of the bentonite and its mineralogy can be critical on clay colloid formation and properties but, so far, their role in this context has not been analysed in detail.

In this study, different smectites or bentonites with high smectite content were selected to determine their main physicochemical properties potentially favouring/hindering colloid detachments from the bulk (erosion). The selection aimed covering a range of possibilities in terms of the smectite content, the composition of the interlayer cations, the clay charge and its distribution between the tetrahedral and octahedral layer.

Colloids were extracted after suspending the different clays in deionized water (DW), to maximize their dispersion, and collecting the supernatant after centrifuging. The mass of dispersed colloids was the first important parameter to assess clay erodibility. Furthermore, the effects of the previously mentioned clay properties on the intrinsic characteristics of the released colloids (size and surface charge) were analysed. Colloid size and surface charge control many important processes as migration, filtration, sedimentation, interaction with rocks and contaminants, thus are fundamental to assess the possible effects of colloids on radionuclide migration. The analysis of clay colloid stability is also an important task, which is detailed in an additional study (Missana et al., 2018).

1.1. Smectite structure and main properties

Smectite clays are 2:1 layer phyllosilicates where two (silica) tetrahedral, τ , sheets sandwich an octahedral, O, sheet forming a TOT structure, or a clay mineral layer (Meunier, 2005; Bergaya and Lagaly, 2013). These clays possess a negative permanent charge which arises from isomorphous substitutions in the phyllosilicate sheets. These substitutions lead to a positive charge deficiency, which is compensated by the presence of cations in the interlayer. In respect to other clays, smectites are characterized by low layer charge, which varies from 0.20e to 0.60e per $O_{10}(OH)_2$ half unit cell (h.u.c), where e is the electron charge ($1.6 \cdot 10^{-19}$ C). This property significantly affects their properties (Mermut and Lagaly, 2001; Christidis, 2008; Sun et al., 2016), especially cation and water retention. In particular, they present large cation exchange capacity (CEC) and good swelling capability. Most of the smectite layer charge is due to the permanent charge, but a small additional contribution (generally < 10%) comes from the amphoteric functional groups at the edges of the clay particles, where Si–O–Si and Al–O–Al bonds are broken and may convert into Si–OH (silanol) and Al–OH (aluminol) groups (Güven, 1988; Tombacz and Szkeres, 2004).

Apart from the degree of substitution, which gives rise to different values of the total layer charge and charge density, the position of the substitutions (in O or τ layer) may play a significant role on the overall

behaviour of the clays (Petit et al., 1998; Hetzel and Doner, 1993; Christidis et al., 2006). With tetrahedral substitution, the charge is much more localized and accessible to cations than octahedral charge, thus exchangeable cations are expected to be more tightly held to the clay surface (Sposito et al., 1999).

Another important property of smectite is the type of interlayer cation balancing the charge deficiency. Different cations with different sizes and hydration energy, are reported to influence several physical properties of the clay including hydration and swelling (Bleam, 1990). The space between clay layers depends on the interlayer cation; for example, Ca^{2+} is a strongly binding ion for clays, because it causes smaller interlayer spacing and gives rise to “more compacted” structure. In general, less hydrated ions bind more strongly than others, like Li^+ or Na^+ . The “double layer” generated by different cations around the clay particles is also different. Na^+ is preferentially distributed over the particle surface whereas Ca^{2+} ions are preferentially located in the interlayer (demixing) (Shainberg and Otoh, 1968).

The presence of Na in the interlayer, approximately above 20%, causes disaggregation of clay platelets and the formation of smaller tactoids, as long reported by different authors (Banin and Lahav, 1968; Shainberg and Kaiserman, 1969; Whalley and Mullins, 1991). Kaufhold and Dohrmann (2008) analysed the capacity of different bentonites to release particles in diluted systems and concluded that Na-rich bentonites released far more colloidal particles than Ca/Mg-rich bentonites.

However, the effects of all these parameter altogether on clay colloidal behaviour and erosion processes have not been investigated so far.

2. Materials and methods

2.1. Clays

Fifteen clays were selected for this work. Most of them are bentonites which have been already studied in the frame of international projects related to HLRW. 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). Additionally, two different saponites (B64, MCA-C) and two low smectite content clays (Ypressian clays) were also included. The clays selected for this study are summarised below.

2.1.1. Seven raw clays

- FEBEX bentonite mined in the 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 was 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). The Wyoming type of bentonite occurs as layers in marine shales, and is widespread and extensively mined, not only in Wyoming but also in parts of Montana and South Dakota.
- Three 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-gray to yellow/red due to the admixture of secondary iron and manganese oxides. The clay referred as to Rokle-S65 (Sabencil) is a fully Na-activated commercial clay (Konta, 1986); the Rokle-B75 is a partially Na activated clay and the Rokle-F0 is untreated.
- Russian bentonite from the Khakassia deposit (Sabodina et al., 2006). This clay is named MSU (the name given by the Moscow State University).

2.1.2. Four commercial dioctahedral smectites

- 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).
- NAl-1 (Clay Mineral Society): it is a *nontronite* i. e. a ferruginous ($4.50 \text{ mmol Fe g}^{-1}$) smectite coming from the Uley Graphite Mine in South Australia (Keeling et al., 2000).
- SAZ-2 (Clay Mineral Society): also known as “Cheto” clay (Jaynes and Bigham, 1987), it is mined in the state of Arizona, USA.

2.1.3. Two trioctahedral smectites (saponites)

- Saponite B64: a Mg-Fe smectite from the Ventzia continental basin at east of Grevena in Macedonia, Greece (Kastridis et al., 2003)
- Saponite MCA-C: a Mg-smectite from Cerro del Aguila-Cerro del Monte from the Cuenca de Madrid Basin, Spain (Cuevas et al., 1993).

Some tests reported here (mainly to analyse the effects on the quantity of smectite in the clay on colloid generation) were carried out with Ypresian clays material (Ondraf-Niras, 2001). The bulk mineralogy of the Ypresian clays is composed of 25%–65% of clay minerals and 35%–75% of non-clay minerals (mainly smectite and illite and in lesser extent chlorite and kaolinite).

2.1.4. Two core samples

- DOEL-40: This core sample (378.78–379.58 m depth) from the Roubaix-Moen Member belongs to ON-Doel borehole drilled in 1998 in the Doel nuclear zone, (Antwerpen, Belgium).
- KALLO-38: This core sample (324.89–325.84 m depth) from the Roubaix/Moen member belongs to ON-Kallo borehole drilled in 2009 in the Kallo town (Beveren, Belgium).

The samples were all used “as-received” and some of them were also exchanged with Na or Ca. To homoionise the clays, they were washed three times with the respective Na/Ca electrolyte (1 M NaClO_4 or Ca $(\text{ClO}_4)_2$) and then washed with deionized water (DW) and DW/ethanol until the electrical conductivity of the suspension was lower than $100 \mu\text{S/cm}$. Afterwards the homoionic clays were dried in the oven and finally powdered in a agate mortar.

2.2. Clay characterization

A complete geochemical and mineralogical characterization was previously carried out by different techniques (XRD, FRX, FT-IR, TG-DSC, TEM-EDS, etc.) 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. For the determination of the crystal chemistry of the clay minerals, the structural formulae and the τ - and σ -charge, high resolution transmission electron microscopy and energy dispersive X-ray energy spectrometry were used. Same techniques and methodologies were applied for all the clays. All the details of this work can be found elsewhere (Fernández et al., 2017).

Commercial bentonites normally contain over 80% of smectite, which is expected to give similar properties from a batch to another. However, in raw bentonites, accessory minerals (feldspars, quartz, cristobalite, gypsum, calcite and pyrite) may vary as well as the presence of other substances such as organic matter or oxides and they may affect the overall colloidal properties of the material.

2.3. Clay colloids

2.3.1. Preparation of colloid suspensions

Colloids were extracted from the different as-received or exchanged clays by dispersing them (1 gL^{-1}) in deionized water (DW) and collecting the supernatant upon centrifuging at approximately 700 g during 10 min. This centrifugation procedure aimed to eliminate particles with size bigger than $1 \mu\text{m}$. The quantity of colloids dispersed from the bulk clay in each case was measured by gravimetry after drying the suspension (50 mL, per triplicate) at 90°C in an oven. DW was used to maximize clay colloid dispersion, under the given centrifugation conditions. The “(maximum) mass of dispersed particles” can be considered the first clay intrinsic property to be considered to evaluate erosion processes.

2.3.2. Water chemical analyses

The initial conductivity and pH of colloid suspensions were measured. Measurements of pH (± 0.10) 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 2.0, 4.0, 7.0 and 10.0. Conductivity measurements were carried out with a Crison EC Meter Basic 30⁺.

A relatively low solid to liquid ratio (1 gL^{-1}) was used to minimize the possible effects of soluble salts present in the clay on the solution chemistry; however, under these experimental conditions, some clay dissolution may occur. The water in equilibrium with the colloidal phase after filtering (by $0.2 \mu\text{m}$) was analysed to determine the presence of different types of ions leached from the clays.

Major and trace cations were analysed by inductively coupled plasma atomic emission spectrometer (Varian 735ES). Sodium and potassium were determined by atomic absorption spectrometry (Varian AA240 FS). Anions were analysed by ion chromatography (DIONEX ICS-2000).

2.3.3. Colloid size determination

The size of clay colloids present in the initial suspension, upon having centrifuged 1 gL^{-1} of clay at 700 g, 10 min, was measured by dynamic light scattering with a Malvern NanoS apparatus with He-Ne laser and at a measurement angle of 173° .

As, under the selected conditions, the effect of water chemistry is minimized, the “initial colloid size” can be considered as an intrinsic colloidal property of the clay. This parameter will be related afterward to other physicochemical characteristics.

2.3.4. Colloid surface charge: electrophoretic mobility measurements

In parallel to colloid size, the intrinsic colloid surface charge was analysed through measurements of particle mobility by Laser Doppler Electrophoresis with a Zetamaster Malvern system equipped with a 2mW He-Ne laser ($\lambda = 633 \text{ nm}$). The electrophoretic mobility can be used to calculate the particle surface potential (ζ -potential) using different approximations (Delgado et al., 2007).

3. Results and discussion

3.1. Clay characterisation

Table 1 shows a summary of the main characteristics of the clays studied in this work (Fernández et al., 2017). In particular, the following parameters are evidenced: the smectite content; the content of Na and main divalent ions (Ca + Mg) in the exchange complex, the charge density, the total layer charge and its distribution between the octahedral and tetrahedral layer.

As can be seen in Table 1, the selection of clays covers a wide range of physicochemical properties. The as-received clays with the highest content in Na are the NANOCOR and MSU, whereas almost pure Ca

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

| Clay | Sm content (%) | Na at exchange sites (%) | Ca + Mg at exchange sites (%) | Layer charge (e/h.u.c) | Charge density (C/m ²) | τ (e/h.u.c) | O (e/h.u.c) |
|----------------------|----------------|--------------------------|-------------------------------|------------------------|------------------------------------|-------------|-------------|
| FEBEX | 94 | 28.0 | 66.4 | 0.38 | 0.13 | 0.06 | 0.32 |
| IBECO | 88 | 26.3 | 69.0 | 0.33 | 0.11 | 0.04 | 0.29 |
| MX-80 | 89 | 68.3 | 26.3 | 0.28 | 0.10 | 0.08 | 0.20 |
| Rokle-F02 | 70 | 0.8 | 92.8 | 0.30 | 0.12 | 0.21 | 0.09 |
| Rokle-B75 | 78 | 55.7 | 34.6 | 0.40 | 0.14 | 0.29 | 0.11 |
| Rokle-S65 | 78 | 76.9 | 16.7 | 0.37 | 0.13 | 0.26 | 0.11 |
| MSU | 79 | 90.2 | 4.46 | 0.35 | 0.12 | 0.14 | 0.21 |
| NANOCOR* | 98 | 93.5 | 2.51 | 0.38 | 0.13 | 0.04 | 0.34 |
| SBI-d-1 (Beidellite) | 78 | 0.7 | 92.0 | 0.32 | 0.11 | 0.26 | 0.06 |
| NAu-1 (Nontronite) | 90 | 3.8 | 91.3 | 0.37 | 0.12 | 0.32 | 0.05 |
| SAz-2 – Cheto | 98 | 0.4 | 92.3 | 0.50 | 0.17 | 0.00 | 0.50 |
| MCA-C (Saponite) | 78 | 4.2 | 87.9 | 0.40 | 0.13 | 0.25 | 0.15 |
| B64 (Saponite) | 65 | 0.3 | 92.3 | 0.51 | 0.17 | 0.13 | 0.38 |
| DOEL-40 | 26 | 47.6 | 34.1 | 0.38 | 0.13 | 0.14 | 0.24 |
| KALLO-38 | 30 | 56.9 | 30.5 | 0.40 | 0.14 | 0.14 | 0.26 |

smectites are SAz-2 and SBI-d-1. The clay with the lowest total layer charge is the MX-80, which presents predominantly octahedral substitutions. On the other hand, the smectite with the highest layer charge is the SAz-2, also with predominant octahedral charge.

The SBI-d-1 and NAu-1 (beidellite and nontronite) have intermediate layer charge values and substitutions mainly in the tetrahedral layer.

The two selected trioctahedral smectites (Saponite B64 and MCA-C) are (Ca, Mg)-type clays. KALLO-38 and DOEL-40 clay rocks have only a small amount of smectite (< 30%), therefore they will not be studied in detail; they will be basically used to understand the possible effect of the quantity of the smectite clay on the generation of colloids.

3.2. Properties of clay colloid suspensions

3.2.1. Contact water chemistry

The characteristics of supernatant of the different colloid suspensions are reported in Table 2. First measurement consisted on the determination of pH and conductivity of the suspensions. Values of pH ranged from 7 to 9.5 and the electrical conductivity from 10 to 90 μS cm⁻¹ approximately. This is a first indication that a different quantity of ion leached from the clays can be present for the different salt inventory and also for some clay dissolution since hydrolysis of clay in contact with deionized water cannot be ruled out.

Table 2

Chemistry of the supernatant of the colloidal suspensions and colloid properties from as-received clays or exchanged clays.

| CLAY | pH | Cond. (μS cm ⁻¹) | I (M) (x 1·10 ⁻⁴) | ppm | ppm/Sm | Size (nm) | Electrophoretic Mobility (μm·s ⁻¹)/(V·cm ⁻¹) |
|----------------------|-----|------------------------------|-------------------------------|----------|--------|-----------|--|
| FEBEX | 8.8 | 25.2 | 2.74 | 166 ± 15 | 177 | 349 ± 1 | -2.18 ± 0.07 |
| IBECO | 8.9 | 44.8 | 3.48 | 157 ± 11 | 178 | 367 ± 5 | -1.80 ± 0.05 |
| MX-80 | 9.4 | 56.8 | 5.11 | 178 ± 12 | 200 | 336 ± 2 | -2.57 ± 0.08 |
| Rokle-F02 | 8.1 | 51.2 | 6.49 | 115 ± 33 | 164 | 288 ± 4 | -1.43 ± 0.04 |
| Rokle-B75 | 7.2 | 21.3 | 2.02 | 124 ± 6 | 159 | 378 ± 9 | -1.50 ± 0.04 |
| Rokle-S65 | 9.1 | 10.9 | 2.85 | 153 ± 19 | 196 | 415 ± 5 | -2.00 ± 0.06 |
| MSU | 8.7 | 28.5 | 5.17 | 263 ± 7 | 333 | 304 ± 8 | -2.37 ± 0.07 |
| NANOCOR* | 7.8 | 40.9 | 10.6 | 720 ± 43 | 735 | 250 ± 10 | -2.96 ± 0.09 |
| SBI-d-1 (Beidellite) | 8.4 | 14.1 | 0.58 | 49 ± 15 | 63 | 700 ± 100 | -2.60 ± 0.15 |
| Nau-1 (Nontronite) | 7.6 | 29.7 | 0.96 | 39 ± 4 | 43 | 783 ± 62 | -2.30 ± 0.11 |
| SAz-2 – Cheto | 8.5 | 14.0 | 0.99 | 61 ± 20 | 62 | 550 ± 100 | -1.47 ± 0.09 |
| B64 (Saponite) | 6.8 | 81.6 | 3.10 | 65 ± 28 | 100 | 553 ± 52 | -1.05 ± 0.03 |
| MCAC (Saponite) | 9.6 | < 10 | nd | 80 ± 12 | 103 | 624 ± 108 | -1.01 ± 0.13 |
| DOEL-40 | 9 | 42.7 | nd | 52 ± 6 | 200 | 531 ± 26 | -1.23 ± 0.04 |
| KALLO-38 | 8.9 | 44.8 | nd | 51 ± 6 | 170 | 250 ± 50 | -2.60 ± 0.08 |
| (Ca)-FEBEX | 6.7 | 14.2 | 2.25 | 47 ± 7 | 50 | 600 ± 15 | -1.3 ± 0.04 |
| (Na)-FEBEX | 7.0 | 11.6 | 2.13 | 321 ± 37 | 341 | 260 ± 10 | -2.50 ± 0.04 |
| (Ca)-IBECO | 7.6 | 32.1 | 4.14 | 71 ± 5 | 60 | 649 ± 40 | -0.75 ± 0.02 |
| (Na)-IBECO | 9.2 | 89.1 | 8.40 | 353 ± 5 | 401 | 284 ± 3 | -2.30 ± 0.07 |
| (Ca)-MX-80 | 9.2 | 14.2 | 1.82 | 53 ± 7 | 59 | 523 ± 25 | -1.18 ± 0.03 |
| (Na)-MX-80 | 8.8 | 12.2 | nd | 600 ± 50 | 674 | 249 ± 10 | -2.70 ± 0.08 |
| (Na)-Rokle-S65 | 8.2 | 67.1 | nd | 394 ± 20 | 505 | 437 ± 10 | -1.85 ± 0.06 |
| (Na)-SBI-d-1 | 8.4 | 14.1 | 1.65 | 412 ± 32 | 528 | 539 ± 9 | -2.71 ± 0.08 |

The initial calculated ionic strength, based on the supernatant chemical analyses, indicated very low salinity in all the cases, with a maximum for NANOCOR* (~1·10⁻³ M) and minimum for the beidellite (~6·10⁻⁵ M), thus aggregation effects for ionic strength should be very limited and that the measured initial size can be considered valid as intrinsic size.

3.2.2. Summary of results

In Table 2 the main characteristics of the colloids extracted from the different clays (as-received and exchanged) are also summarised. In particular, the following parameters will be discussed in detail: a) the concentration of colloid dispersed from the clay (normalized or not to the smectite content of the clay); b) the initial particle size; c) the initial electrophoretic mobility (EM).

3.3. Analysis of parameters affecting colloid formation and colloid properties

The first important data to be analysed is the mass of colloids obtained upon centrifuging, which provides the first indication on the capability of the different clays to disperse colloidal particles under the most favourable chemical conditions (DW).

From Table 2 it is immediately clear that Na-clays released higher

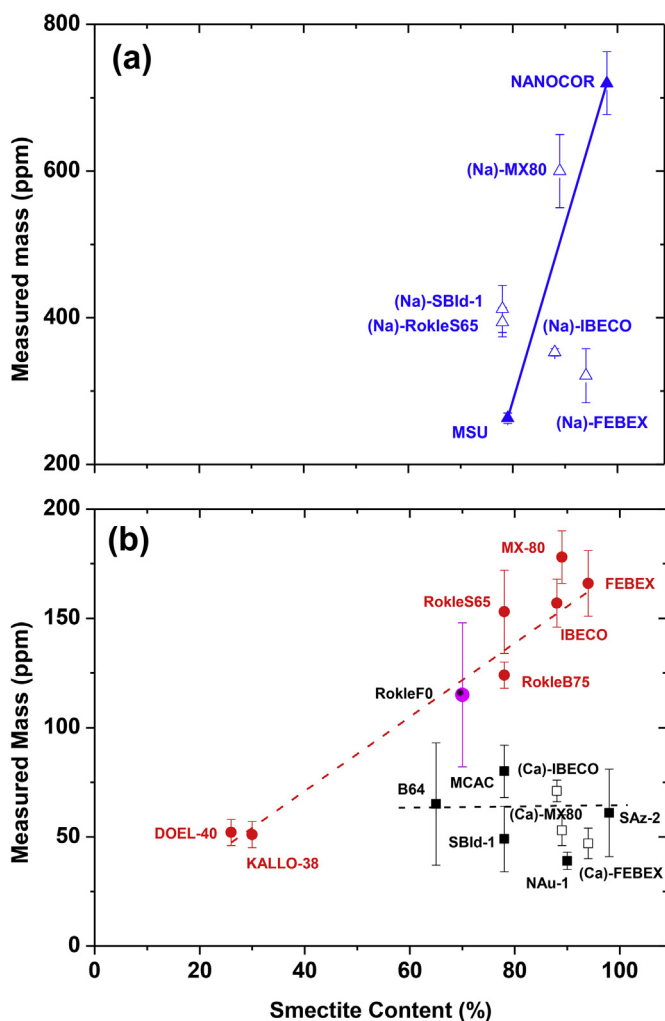


Fig. 1. Mass of the colloid generated upon centrifugation as a function of the clay smectite (Sm) content. (a) Na-clays (▲); (b) (Ca,Na) mixed clays (●) and Ca-clays (■). Open symbols refer to exchanged clays.

masses of colloids than Ca-clays. As already mentioned in the Introduction section, Na is known to favour the dispersion of clays. Thus, as expected, the capability of the clays of releasing colloids is related to the composition of the exchanging cations. Therefore to facilitate the comparison and analyses of all the data, the clays were first classified considering the composition of their interlayer cations. *Na-type clays* will be defined those with Na > 80% and Ca + Mg < 10% (blue triangles in the graphs); *Ca-type* those with Ca + Mg > 70% and Na < 10% (black squares in the graphs); *(Na,Ca)-mixed type* clays those with other intermediate Na/Ca values (red circles in the graphs). Exchanged clays are represented in the graphs with open symbols. When the clays were homoionised, for simplicity, the content of the exchangeable cation was considered 100%.

3.3.1. Role of smectite and Na content

Fig. 1 shows the mass of colloids, generated from the clays upon centrifugation, as a function of the smectite content for: a) Na-clays, b) (Na,Ca)-mixed and Ca-clays. As already observed, the quantity of colloids generated from Na-clays (scale 200–800 ppm) is significantly higher than in (Na,Ca)-mixed and Ca-clays (scale 0–200 ppm), and this point will be discussed in detail in the next Figure.

In (Na, Ca)-mixed and Na-clays, the mass of colloids tends to increase as the smectite content increases. The samples KALLO-38 and DOEL-40 with a quite low smectite content (< 30%) generated a small quantity of particles (Fig. 1b), despite their relatively high content of

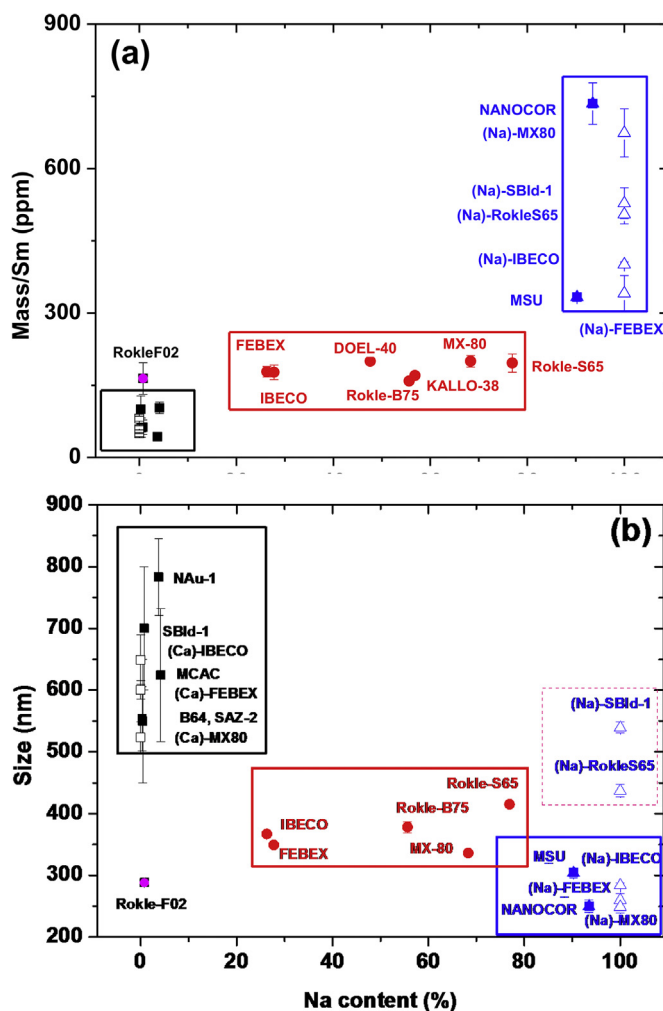


Fig. 2. (A) Colloid mass normalised to Sm content and (b) intrinsic hydrodynamic size of colloids as a function of the content of Na (%) as interlayer cation (▲). Na-clays (●); (Ca,Na) mixed clays and (■) Ca-clays. Open symbols refers to exchanged clays. Labels of Ca-clays were eliminated because hardly readable.

exchangeable Na (48–57%).

Instead, no such dependence was observed for Ca-clays, which in fact shows similar values of colloid generated independent of the smectite content of the clay.

Amongst Ca-clays, the sample Rokle-F0, presents an anomalous behaviour because it shows a relatively high mass of colloid generated, comparable to that of (Na,Ca)-mixed clays. The detailed characterisation of this material (by microscopic techniques with associated microanalyses techniques (SEM, TEM) and X-ray diffraction) showed a large amount of iron oxides that can bias the analysis of the colloids produced by the material (for this reason it will be differentiated in the graphs).

Alonso et al. (2013, 2018) also observed a certain dependence of the colloid release on the smectite content in erosion experiments with compacted and confined clays. As the quantity of smectite might be relevant on mass loss in many cases, a normalization of the mass of colloid generated in respect to the smectite content will be done (ratio between colloid mass, in ppm, and the percentage of Sm) for generalizing the data and referring them to the main mineral of interest.

Fig. 2 shows the colloid mass released, normalized to the Sm content (Fig. 2a), and the colloid size (Fig. 2b) as a function of the percentage of Na as interlayer cation.

Data of both colloid mass and colloid size are distributed in three

clearly defined zones. Na-clays release the highest colloidal mass (from 350 to 750 ppm approx.); all (Na, Ca)-mixed clays generate a very similar quantity of colloids (from 150 to 200 ppm approx.) and, finally, the mass of colloids generated by Ca-clays (from 40 to 150 ppm) is always lower than that of (Na,Ca)-mixed clays. For what concerns particle size, the highest colloid sizes (> 500 nm) corresponds to Ca-clays, thus the presence of Ca as exchangeable cation above the 80%, clearly favours the formation of large particles. However, as the percentage of Na as exchange cation is above 20%, a clear drop in colloid size occurs. The size of all the (Na,Ca)-mixed clays is similar, within the range of 350–450 nm. Finally, most of the Na-clay colloids have a size around 250–300 nm.

Within this clear picture, some exceptions can be depicted. The first, is the sample Rokle-F02, a Ca-clay, showing colloids with size lower than 300 nm. This sample was observed to be “anomalous” also in the analysis of colloid generation (Fig. 1b), and also for what concerns its colloid size, it can be most probably related to its high iron oxy-hydroxides content.

The others are the (Na)-RokleS65 and (Na)-SBId-1, which show sizes bigger than the (Ca,Na)-mixed clays even when they are Na-exchanged. In particular, it is interesting observing in Fig. 2 that, even if three zones can be clearly distinguished, a significant spread of data is observed especially for Na-clays, in the case of colloid mass (Fig. 2a) and for Ca-clays, in the case of colloid size (Fig. 2b). This result suggests that, even if the Na/Ca content as interlayer cations is a fundamental parameter controlling colloid dispersion and colloid size, other factors must be relevant on colloid release and on their intrinsic size.

Fig. 3 shows the intrinsic electrophoretic mobility (EM) of the different clay colloids as a function of Na content as interlayer cation. EM data are expressed as $(\mu\text{m}\cdot\text{s}^{-1})/(\text{V}\cdot\text{cm}^{-1})$. The mobility of 2:1 clays is always negative, according to their negative permanent charge (Sondi et al., 1996; Thomas et al., 1999; Luckam and Rossi, 1999) thus, decreases and increases in EM are referred to absolute values.

Ca-clays present the smallest values of EM (-0.5 to -1.5 $(\mu\text{m}\cdot\text{s}^{-1})/(\text{V}\cdot\text{cm}^{-1})$), except for beidellite (SBId-1) and nontronite (NAU-1) that show significantly higher values than others Ca-clays. However, when the content of Na in the exchange complex exceeds 20% a slight increase in EM is seen. A content of Na above a 20% is enough to provide, in most cases, EM values similar to those of Na-clays (-2 to -3 $(\mu\text{m}\cdot\text{s}^{-1})/(\text{V}\cdot\text{cm}^{-1})$). The highest intrinsic EM value has been measured for the sodic NANOCOR® clay, which is an almost pure Na-smectite and with the charge mostly located in the octahedral layer. Results show

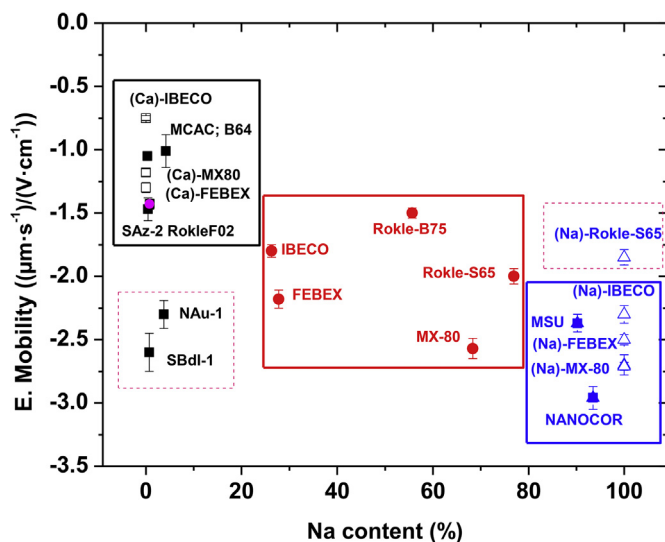


Fig. 3. Intrinsic electrophoretic mobility as a function of the Na content (%) as interlayer cation (\blacktriangle). Na-clays (\bullet); (Ca,Na) mixed clays and (\blacksquare) Ca-clays. Open symbols refers to exchanged clays.

that colloid EM is sensitive to the valence of the main ion adsorbed on the clay, as previously reported (Bar-On and Shainberg, 1970).

However, the intrinsic EM of all the clays ranges from approximately -1 to -3 $(\mu\text{m}\cdot\text{s}^{-1})/(\text{V}\cdot\text{cm}^{-1})$. This variation is not very large, which suggests that this parameter may not be very significant for establishing the stability behaviour of the different clay colloids.

Additionally, also in the case of EM measurements, a certain spread is observed for clays of the same type, indicating again the possible relevance of other parameters than Na/Ca content on colloid EM (and ζ -potential).

3.3.2. Role of total layer charge and charge distribution

To understand the observed difference on the intrinsic colloidal properties of clays with similar Na/Ca content, the effects of clay total charge and charge distribution (τ vs. O), will be investigated. In general, surface charge density data (in C/m^2 , reported in Table 1) gave similar information as that provided by total layer charge data, thus they will be not reported here.

Fig. 4 shows the mass of colloid (normalised to the Sm content) generated from the different clays, as a function of the total layer charge (Fig. 4a) and the tetrahedral charge (Fig. 4b). For (Na,Ca)-mixed and Ca-clays, the detached colloidal mass does not depend neither on the layer charge nor on its distribution. Thus, the divalent ion content (Ca + Mg) in the interlayer, when it is high enough (15–20%), becomes a dominating factor for particle release because it strengthens the bonds between clay particles, controlling and limiting their release, in spite of the magnitude of the clay charge and charge distribution.

On the other hand, Na-clays behave differently. Even if the experimental data are a bit scattered, clear tendencies can be detected. The mass of colloid generated from Na-clays decreases when the total layer charge increases and when the tetrahedral charge decreases. The increase in total layer charge should favour the overall retention of the exchangeable cations on the particles surface, thus hindering the detachment of the particle from the bulk, as observed in Fig. 4a. Similarly, an increase in τ charge should favour a stronger adsorption of the exchanging cations and an increase of the interactions between the TOT layers, then making more difficult the particle release. Therefore it is not clear at this point why, when τ charge increases more colloidal mass is released (Fig. 4b). This will be explained later.

In Fig. 4, an anomalous behaviour is detected for NANOCOR® and (Na)-MX-80, which produced significantly higher colloid mass than the others, in relation to their total layer charge and/or tetrahedral charge. It seems that the combination of various factors as, very high Na and smectite content, low total charge and (in principle) low τ , should intensify particle detachment. However, other factors could be of importance and should also be investigated; in particular, all the potential effects related to the chemistry of the solution.

Precisely, the NANOCOR® clay, presents a quite high content of sulfates (Fernández et al., 2017) which are released in solution when it is dispersed. Sulfate is an adsorbing ion that can neutralize the positive charge at the edges of the clay particles and this might reduce the edge-face, EF, interactions and, therefore, enhance the release of colloids.

Fig. 5 shows the data of the hydrodynamic size of the clay colloids as a function of the total layer charge (left) or the tetrahedral charge (right). Fig. 5a,d shows the data for Ca-clays, Fig. 5b,e the data of (Na,Ca)-mixed clays and Fig. 5c,f data for Na-clays. In this Figure it can be observed that the size of the released colloids does not clearly depend on the layer charge. Therefore this is not a significant parameter in relation to colloid size.

On the other hand, for all the types of clays, the size of the particles tends to increase when the tetrahedral charge increases. The stronger bonds between interlayer cations and clay surface, promoted by high τ , favour the formation and release of larger colloids. This is very interesting result, indicating that the smectite particle delamination is dependent on the magnitude of the tetrahedral charge and that even if the presence of divalent cations is a dominating factor on the formation of

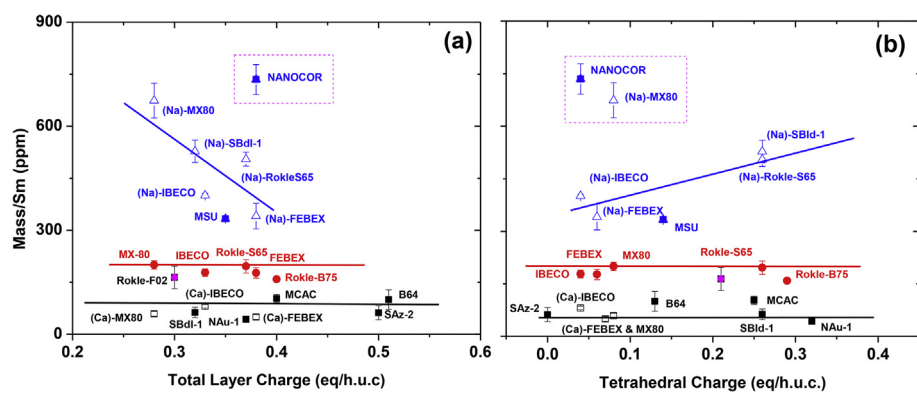


Fig. 4. Normalized colloid mass as a function of (a) the total layer charge and (b) the tetrahedral charge (▲). Na-clays (●); (Na,Ca) mixed clays and (■) Ca-clays. Open symbols refer to exchanged clays.

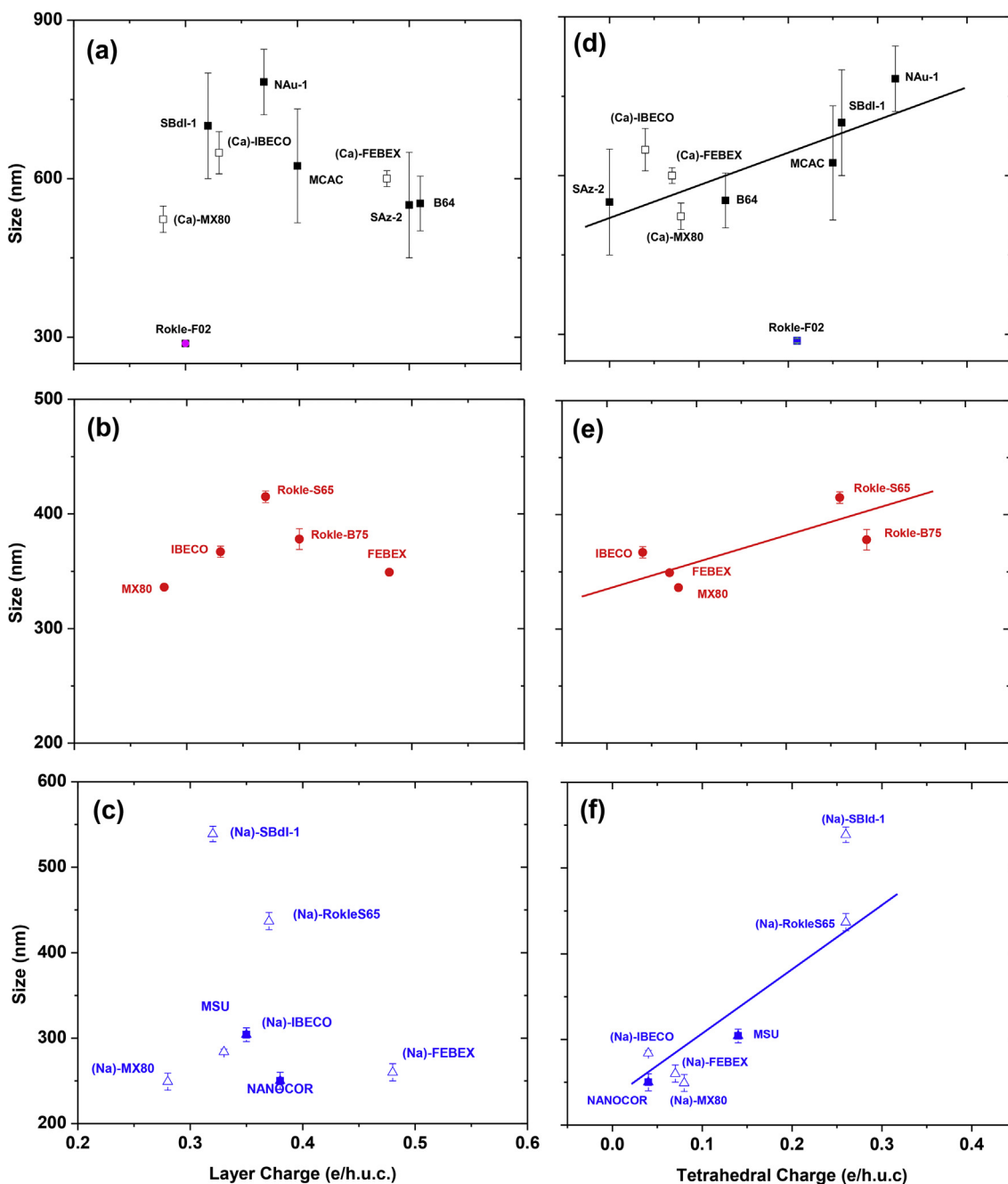


Fig. 5. Intrinsic hydrodynamic size of colloids as a function of the total layer charge (left) or tetrahedral charge (right) for (a,d) Ca-clays (■); (b, e) (Na,Ca)-mixed clays (●) and (c,f) Na-clays. Open symbols refer to exchanged clays.

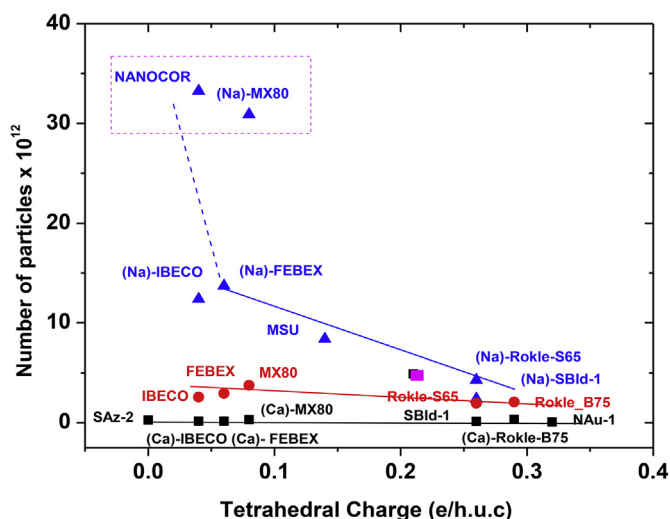


Fig. 6. Number of particle released as a function of the tetrahedral charge (▲). Na-clays (●); (Ca,Na) mixed clays and (■)Ca-clays.

big colloids, the location of charge in the smectite structure is also fundamental.

Besides, this result explains very well why in dispersive Na-clays, the detached colloid mass increases when increasing τ charge (Fig. 4b), in spite of the expected stronger interactions between TOT layers. The fact that colloid mass increases, does not mean that more colloids are released, yet larger colloids are formed, which have larger volumes and weigh more.

To clarify this point, Fig. 6 shows the number of released particles per liter which can be calculated considering the ratio between the total colloid mass (gL^{-1}) and the volume of a particle (cm^3).

Particle volume was calculated, for simplicity, assuming spherical particles with the measured hydrodynamic diameter $V = \frac{4\pi(R_H)^3}{3}$; the same specific density for all the clays (2.7 gcm^{-3}) was considered. The hydrodynamic radius (R_H , nm) is taken from data of Table 2.

Fig. 6 demonstrates that the number of released particles effectively decreases when τ charge increases and that, in effect, the mass released increase just because colloid size is increasing. Particles can be released because Na as main interlayer cation is not able to produce bonds strong enough with the bulk material.

Finally, Fig. 7 shows the EM of clay colloids as a function of the tetrahedral charge for Na-clays (Fig. 7a); (Na,Ca)-mixed clays (Fig. 7b) and Ca-clay (Fig. 7c). The Figure shows that for all the clay types there is a certain tendency of EM to decrease when tetrahedral charge increases. Strong interactions between the interlayer cations (especially Ca) provoke a better neutralization of the layer charge reflected in a diminution of the EM. The charge located in tetrahedral layers is more accessible to exchangeable cations therefore it is better neutralised by cations (especially divalent), thus if τ increases the apparent surface potential is expected to be less negative.

In this case, the exceptions are: the nontronite, NAu-1, and the beidellite, SBdl-1, both *as-received* and in its Na-form which, in spite having high tetrahedral charge present amongst the highest EMs. The reason why this occurs is not totally clear at the moment. Nevertheless, it can be pointed out that, these two clays form very large particles and sometimes gels that make difficult the electrokinetic measurements.

Besides, the particles generated from these clays are especially large: it might be an indication that large EF aggregated are formed where, most probably, cation adsorption and charge compensation may suffer kinetic effects more pronounced than in face-to-face, FF, aggregated.

On the other hand, no clear dependence of EM on the total layer charge and charge density could be observed. Other authors (Shainberg

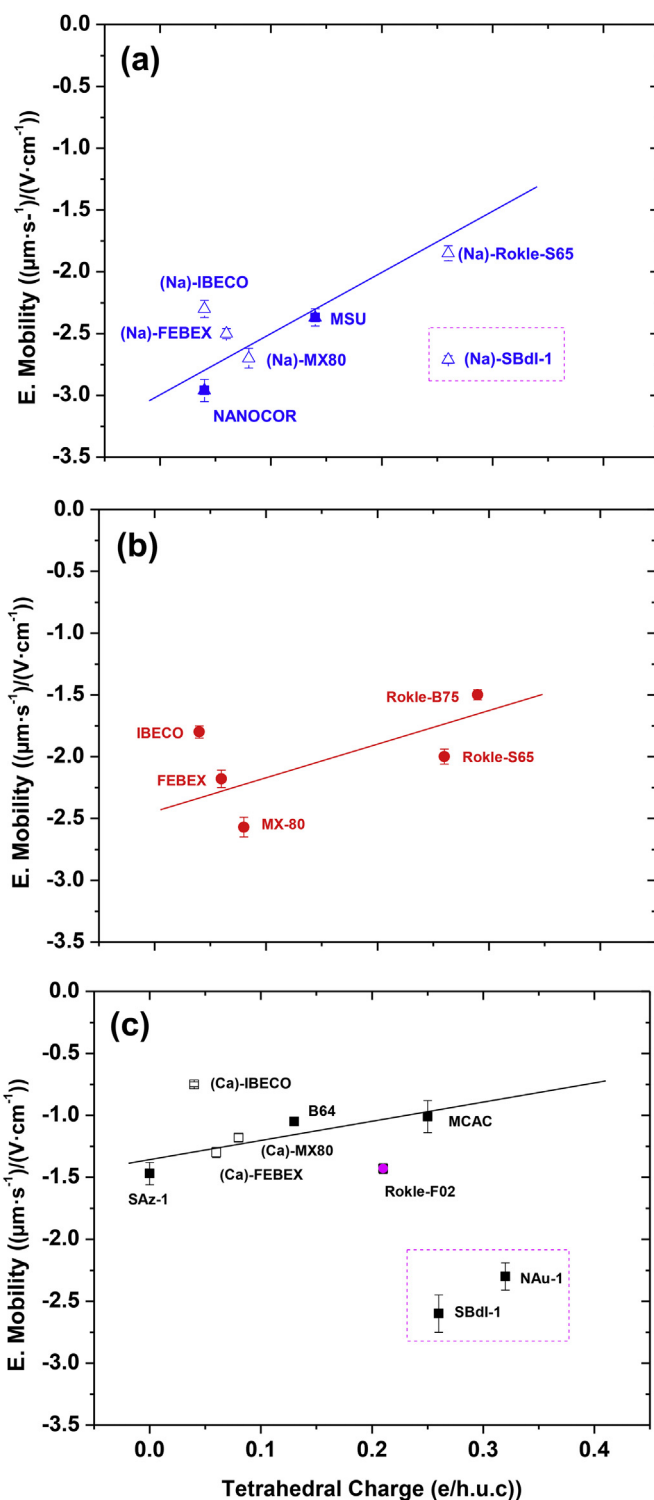


Fig. 7. Intrinsic electrophoretic mobility of clay colloids as a function of the tetrahedral charge (▲). Na-clays (●); (Ca,Na) mixed clays and (■) Ca-clays. Open symbols refer to exchanged clays.

and Kaiserman, 1969) analysed the effects of layer charge on the electrophoretic mobility of smectite; they found that the layer charge did not largely influence the EM of smectite at neutral to alkaline pH.

3.4. Implications for bentonite erosion in HLRW repositories

The selection of the clay as engineered barrier for a high level waste repository must consider several factors to guarantee its safety at the

long term. The relation between bulk physicochemical properties and the intrinsic characteristics of the released clay colloids gives important informations on barrier erodibility.

Results presented in this work showed that Na-clays with high smectite content and low total layer charge are those able to better disperse colloids. Therefore, to minimise the mass loss, the clay should not contain more than 80% of Na in the exchange complex. It has to be taken into account that the enhanced dispersion of colloids from Na-clays is also significantly affected by charge location. As observed in Fig. 6, an increase of τ inhibits particle release but also an increment of the size of generated colloids (Fig. 5 b,d,f), that in the case of Na-clays induces an overall increase of the colloid mass release (Fig. 4b). As this effect is appreciable in Na-clays, this confirms that bentonites for engineered barrier should not high quantities of exchangeable Na.

Calcium as interlayer cation is able to produce very strong interactions between TOT layers and, when present in high enough concentration, dominates over other effects that can be induced by charge (both magnitude and location). Thus, the presence of Ca is fundamental to limit clay erosion.

The release and/or transport of bentonite colloids in fractures has been analysed in the past (Möri et al., 2003; Schäfer et al., 2004; Missana et al., 2008; Lahtinen et al., 2010; Albarran et al., 2011), and in most of the cases, their unretarded migration has been proven, even if filtration of a large part of their mass was also observed, especially in experiments with large residence times. The possible role of eroded clay colloids on radionuclide migration is controlled by many factors as: colloid velocity in the fracture, deposition/filtration during transport (colloid–rock interactions) and colloid stability (colloid–colloid interactions).

Yet, all these factors depend on colloid characteristics (size and charge) and the chemistry of the system (Schäfer et al., 2012; Honeyman, 2001). Brownian diffusion and sedimentation which basically depends on particle size in a complex way (Bradford et al., 2002; Zvikelsky and Weisbrod, 2006; Albarran et al., 2013) are the main processes controlling migration and deposition. Brownian diffusion is important for small particles, whereas sedimentation is favored for big or high density colloids. Big particles may suffer exclusion processes and present retardation factors (R_p) significantly smaller than that of conservative tracers (Albarran et al., 2013) but also higher probability of sedimentation.

In the present study, it has been shown that, in general, Ca-clays produced colloids with the largest sizes, and Na-clays the smallest. However, colloid size is also controlled by the clay charge location: an increase in τ produced an increase in colloid size, independent of the main interlayer cation.

The surface charge of all clay particles is always negative due to their negative permanent charge. Colloid aggregation is mainly controlled by their surface potential, the higher the potential, the higher repulsive forces preventing aggregation. Ca-clays showed the lowest values of EM and, in general, EM for clay colloids, decreased when τ increased, exceptuating for two samples (Fig. 7). However, the intrinsic EM of all the clay particles was not very high and not very different from clay to clay (from approximately -1 to -3 ($\mu\text{m s}^{-1}$)/(V $\cdot\text{cm}^{-1}$)). For this reason, their aggregation behaviour in groundwater is not expected to be very different from clay to another, even when other intrinsic colloidal properties have been shown to be quite different. A parallel work on clay colloid stability is being done to confirm this hypothesis (Missana et al., 2018).

In the present study, the tests were performed using deionised water and a relatively low solid to liquid ratio, to maximise the formation of colloids and to minimise the chemical effects that can influence the intrinsic properties of the different clay colloids. Nevertheless even in these diluted conditions, the chemical environment generated by each clay is different. This is a very important point to be accounted for analysing formation and stability of clay colloids when, as occurs in repository conditions, the solid to liquid ratio is much higher. Under the

frame of the European BELBAR project, it was found that salinity higher than 10–20 mM (Na) might completely inhibit the erosion process (Missana, 2016; Schatz et al., 2016).

The NANOCOR[®] clay, which has been shown to have a high capability for colloid generation, contributes more than the others to the increase of salinity of the water in contact (Table 2). The analysis of its chloride and sulphate inventory (Fernández et al., 2017) shows that it is significantly higher ($\text{Cl}^- = 4.4$ and $\text{SO}_4^{2-} = 10.68$ mmol/100 g) than that of other clays, for example, IBECO ($\text{Cl}^- = 1.82$ and $\text{SO}_4^{2-} = 1.35$ mmol/100 g) or Febex ($\text{Cl}^- = 3.0$ and $\text{SO}_4^{2-} = 0.78$ mmol/100 g) probably due to the treatment performed for purifying/exchanging it.

The determination of the clay salt inventory and the analysis of clay/water interactions are therefore very important. The clays containing the higher amount of soluble salts (either naturally or due to other treatments) will especially affect the chemical characteristics of the water in contact, when present at high solid to liquid ratio. Thus, the possible water/clay interactions must be accounted for in the overall discussion of the properties affecting erosion under repository conditions (Alonso et al., 2018).

4. Conclusions

The colloidal fraction ($< 1 \mu\text{m}$) of different clays was obtained suspending 1 gL⁻¹ of solid in deionized water and collecting the supernatant after centrifuging. The mass of colloids present in the supernatant provided the first indication of the clay erodibility. Afterwards, the dispersed colloids were characterised measuring their size and electrophoretic mobility. The properties of colloid generated from the different clays were related to the clay bulk properties, in particular: the smectite content, the composition of interlayer cations, the total layer charge and its distribution between the tetrahedral and octahedral layer.

The presence of Na as interlayer cation ($> 80\%$) was observed to be the main factor enhancing the dispersion of colloids from the bulk material. Furthermore, colloids from Na-clays, in general showed the smallest size with the highest EM.

Charge distribution was also observed to play a role on the characteristics of colloids. An increase of the clay tetrahedral charge produced an increase of colloid size independently of the main interlayer cation; furthermore, for all the clay types, an increase of tetrahedral charge could be related to a decrease in EM.

Calcium as exchangeable cation enhances the bonds between TOT layers and its presence can be dominant over other effects induced by the clay charge. Indeed, the presence of Ca is critical to limit clay erosion.

The erosion of the bentonite barrier due to chemical or physical agents must be minimised; therefore the knowledge of the colloidal properties of the smectite as well as of the clay/water interactions that could affect them are fundamental issue to be accounted for. The studies performed here are also basic to interpret the results of erosion tests carried out with compacted and confined bentonite.

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