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**Addition of Al<sub>2</sub>O<sub>3</sub> nanoparticles to bentonite: effects on surface charge and Cd sorption properties**

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**ABSTRACT**

Compacted bentonite barrier in radioactive waste repositories is expected to prevent radionuclide migration, due to its high sorption capability for many radionuclides. This study analyses whether the addition of Al<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) enhances the sorption properties of bentonite. The study was carried out with <sup>109</sup>Cd, highly pollutant heavy metal and divalent fission product. Sorption experiments were conducted in NaClO<sub>4</sub> at different ionic strengths (5 · 10<sup>-4</sup> to 10<sup>-1</sup> M) and pH (2 to 10), using mixtures of sodium homoionised bentonite and Al<sub>2</sub>O<sub>3</sub> in different proportions.

It has been probed that addition of Al<sub>2</sub>O<sub>3</sub> NPs to bentonite enhances Cd sorption at pH higher than 6. The effect of Al<sub>2</sub>O<sub>3</sub> NPs addition on the surface properties of bentonite colloids was also analyzed by measuring particle size and surface charge in all studied systems.

**INTRODUCTION**

Bentonite clay, mainly composed by smectite, is a buffer and backfill material considered in nuclear waste repositories, owing to its swelling properties and high sorption capability for many radionuclides. When hydrated, smectite particles take on a permanent negative surface charge that promotes retention of positively charged ions, while radionuclides whose dominant aqueous species were anionic can be mobile. The charge on the edge of bentonite particles is positive or negative, depending on pH conditions.

The aim of this study is to evaluate whether the addition of Al<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) enhances the sorption properties of bentonite. The addition of nanoparticles (diameters < 50 nm) positively charged may favour the sorption of negatively charged species or modify sorption of cations. The enhancement of bentonite sorption properties has been tested with magnetic Fe nanoparticles, promoting contaminant reduction [1, 2], but no previous study with Al<sub>2</sub>O<sub>3</sub> was reported.

FEBEX clay, a Spanish Ca-Mg bentonite, was selected for the study [3]. The FEBEX clay was homoionised in Na (Na-bentonite) and mixed at different weight proportions with Al<sub>2</sub>O<sub>3</sub> NPs (nominal size < 50 nm), in NaClO<sub>4</sub> at different ionic strengths. The surface properties (size and surface charge) of the independent Na-bentonite clay and Al<sub>2</sub>O<sub>3</sub> NPs suspensions and of the bentonite /Al<sub>2</sub>O<sub>3</sub> mixtures were analysed. In the binary systems interaction of particles with very different surface charge properties may promote changes in charge or particle coagulation that affects contaminant retention, as previously observed for hematite, magnetite and TiO<sub>2</sub> /clay mixtures [4, 5].

The sorption properties of the Na-bentonite /Al<sub>2</sub>O<sub>3</sub> mixtures were evaluated with <sup>109</sup>Cd(II). Cadmium is a heavy metal of great environmental concern that has a low fission product yield, whose dominant aqueous species are positive. Previous studies on Cd sorption

onto bentonite [6, 7, 8, 9] or alumina are reported [10, 11], but no previous study with bentonite / Al<sub>2</sub>O<sub>3</sub> mixtures is available.

## EXPERIMENTAL DETAILS

### Materials

The bentonite selected is the FEBEX clay, a Ca-Mg bentonite from Spain [1]. The cation exchange capacity (CEC) of FEBEX clay is 102 ± 4 meq/100g and the BET surface area is 33 m<sup>2</sup>/g [12]. FEBEX bentonite was purified and homoionized with Na (Na-bentonite) by washing three times with 1 M NaClO<sub>4</sub>. The colloidal fraction (size smaller than 500 nm) was obtained by centrifuging several times the suspension at 600 × g during 10 min and collecting the supernatant. Samples were equilibrated by dialysis with NaClO<sub>4</sub> electrolyte at the desired ionic strength.

The Al<sub>2</sub>O<sub>3</sub> nanoparticles (NPs), whose phase is γ-Al<sub>2</sub>O<sub>3</sub>, were prepared in NaClO<sub>4</sub> electrolytes without previous cleaning procedure from Al<sub>2</sub>O<sub>3</sub> nanopowders with a nominal size < 50 nm (Aldrich) and a with a BET surface area of 136 m<sup>2</sup>/g.

Four different suspensions were prepared varying the percentage in weight: Na-bentonite 100 %, Na-bentonite / Al<sub>2</sub>O<sub>3</sub> 50:50 %, Na-bentonite / Al<sub>2</sub>O<sub>3</sub> 10:90 %, and Al<sub>2</sub>O<sub>3</sub> 100%, prepared in NaClO<sub>4</sub> electrolytes. For characterisation and stability studies, a solid to liquid concentration of 10 mg/L was considered, while sorption experiments were carried out with 0.5 g/L.

Cadmium solution was prepared in HCl 0.1 M from a commercial <sup>109</sup>CdCl<sub>2</sub> (Ecker & Ziegler) solution bearing a carrier ([Cd]<sub>TOT</sub> = 4.45 · 10<sup>-3</sup> M, [<sup>109</sup>Cd] = 3.54 · 10<sup>-6</sup> M). For sorption experiments the final Cd concentration used was 4.6 · 10<sup>-8</sup> M.

Cd speciation in NaClO<sub>4</sub> was analysed with the CHESS code [13]. The predominant aqueous specie up to pH 8 is Cd<sup>2+</sup> and at alkaline pH the hydrolysed species CdOH<sup>+</sup> and Cd(OH)<sub>2</sub>(aq) dominates. For pH > 11 the anionic species Cd(OH)<sub>4</sub><sup>2-</sup> and Cd(OH)<sub>3</sub><sup>-</sup> may have some influence. No Cd precipitation under the experimental conditions is expected.

### Suspensions characterization

The surface characteristics of the suspensions were studied as a function of pH and ionic strength. Photon Correlation Spectrometry (PCS) technique was used to measure the mean particle size, using a Zetasizer Nano S Malvern Instrument of wavelength λ = 633 nm equipped with a photomultiplier at 173°.

To evaluate the surface charge of the particles, zeta potential (ζ) was measured by Laser Doppler electrophoresis with a Zetamaster Malvern system equipped with a Spectra-Physics 2mW He-Ne laser (λ = 633 nm). The electric conductivity of the samples was always checked upon HCl or NaOH addition to detect changes in ionic strength. For 4 ≤ pH ≤ 10 increase in ionic strength is expected.

### Sorption experiments

Sorption edges were carried out at room temperature under oxic conditions, in the independent suspensions and Na-bentonite / Al<sub>2</sub>O<sub>3</sub> mixtures, by changing the pH from pH 2 to 12, adding NaOH or HCl 0.1 M. Sorbent total concentration in all experiments was 0.5 g/L, and total cadmium concentration was fixed to 4.6 · 10<sup>-8</sup> M.

Samples were maintained in polyethylene tubes (10 mL) in agitation during one week. After that samples are centrifuged (21275 g, during 1 hour) to separate the liquid from the solid. Three aliquots (2 mL) of the supernatant are sampled and <sup>109</sup>Cd activity is measured with a Packard Autogamma COBRA 2 counter.

Distribution coefficients (K<sub>d</sub>) were calculated from the three aliquots of the supernatant with this equation:

$$K_d = \frac{C_i - C_f}{C_f} \cdot \frac{V}{m} \quad \text{Eq (1)}$$

where C<sub>i</sub> is the initial activity (counts/ml), C<sub>f</sub> the final activity in the supernatant (counts/ml), m is the mass of the solid (g) and V the liquid volume (mL).

On Al<sub>2</sub>O<sub>3</sub> system, Cd sorption on tube walls was estimated considering that sorption on oxides at lower pH (2-5.5) values should be null and 7% of the initial Cd concentration was subtracted.

## RESULTS

### Suspensions characterization

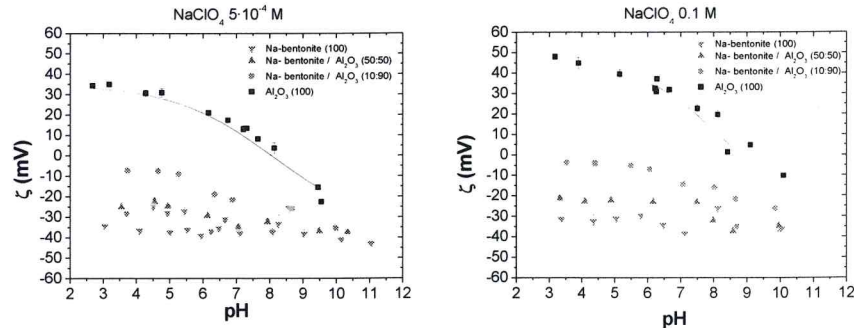
Figure 1 shows the zeta potential (ζ) measured on independent Na-bentonite (100) and Al<sub>2</sub>O<sub>3</sub> (100) suspensions and on Na-bentonite / Al<sub>2</sub>O<sub>3</sub> mixtures (50:50 and 10:90). Only figures at 5 · 10<sup>-4</sup> M (left) and 10<sup>-1</sup> M (right) ionic strength are shown, but similar behaviour was found for 10<sup>-2</sup> M and 10<sup>-3</sup> M.

In Figure 1 it can be appreciated that the zeta potential of Na-bentonite is always negative (ζ ≈ -35 mV) almost independent of pH or ionic strength [14]. The zeta potential of Al<sub>2</sub>O<sub>3</sub> depends on pH, being positive for acidic pH and negative for pH higher than the isoelectric point (IEP). The Al<sub>2</sub>O<sub>3</sub>/bentonite mixtures, showed negative ζ values, within the whole pH range that are lower than those of bentonite for pH values lower than the isoelectric point of Al<sub>2</sub>O<sub>3</sub>: This behaviour was equivalent at all studied ionic strengths. The different charge of the mixed systems may affect the retention of contaminants.

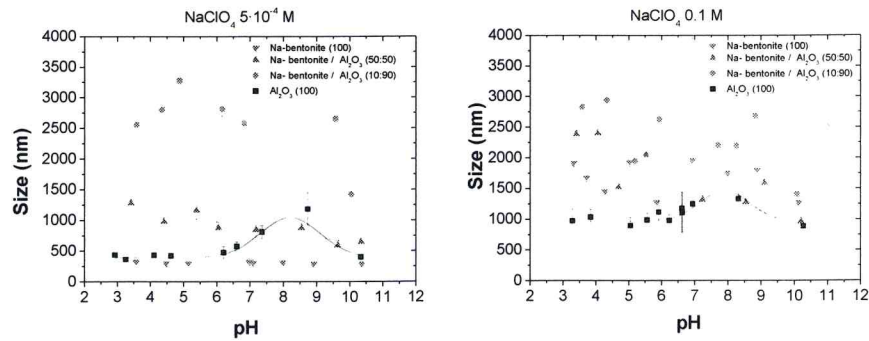
Figure 2 shows the average size of particles measured by PCS on the independent Al<sub>2</sub>O<sub>3</sub> and Na-bentonite suspensions and on Na-bentonite / Al<sub>2</sub>O<sub>3</sub> mixtures, as function of pH, at 5 · 10<sup>-4</sup> M (Figure 2 left) and 10<sup>-1</sup> M (Figure 2 Right). Measurements were carried out after ultrasonication treatment for five minutes once pH was fixed. Equivalent behaviour was found for 10<sup>-2</sup> M and 10<sup>-3</sup> M ionic strengths (I).

The initial average size of bentonite colloids in NaClO<sub>4</sub> 5 · 10<sup>-4</sup> M is around 300 nm (Figure 3 Left) and independent of pH. This average size remains practically unvaried up to I = 1 · 10<sup>-3</sup> M, but at I = 10<sup>-1</sup> M bentonite colloids are completely destabilized (size > 1500 nm in Figure 2 right).

As expected, the average size of the Al<sub>2</sub>O<sub>3</sub> suspension showed dependence on pH, with the maximum size corresponding to the isoelectric point (IEP), pH ≈ 8-9, where aggregation is promoted [15, 16]. Far from the IEP and at low ionic strength, the average size was 425 ± 40 nm, indicating that Al<sub>2</sub>O<sub>3</sub> NPs are stable as nanoaggregates (nominal size of 50 nm confirmed by AFM measurements). The average particle size increases up to 540 nm at 10<sup>-3</sup> M, 610 nm at 10<sup>-2</sup> M and 1000 nm in 10<sup>-1</sup> M (Figure 3 Right).



**Figure 1.** Average zeta potential as a function of the pH at (Left)  $5 \cdot 10^{-4}$  M and (Right)  $10^{-1}$  M, for  $\nabla$  Na-bentonite (100),  $\blacktriangle$  Na-bentonite /  $\text{Al}_2\text{O}_3$  (50:50),  $\bullet$  Na-bentonite /  $\text{Al}_2\text{O}_3$  (10:90),  $\blacksquare$   $\text{Al}_2\text{O}_3$  (100). Lines depict the tendency of experimental data.



**Figure 2.** Average particle size measured by PCS as a function of the pH in  $\text{NaClO}_4$  (Left)  $5 \cdot 10^{-4}$  M and (Right)  $10^{-1}$  M, for  $\nabla$  Na-bentonite (100),  $\blacktriangle$  Na-bentonite /  $\text{Al}_2\text{O}_3$  (50:50),  $\bullet$  Na-bentonite /  $\text{Al}_2\text{O}_3$  (10:90),  $\blacksquare$   $\text{Al}_2\text{O}_3$  (100). Lines show the tendency of experimental data.

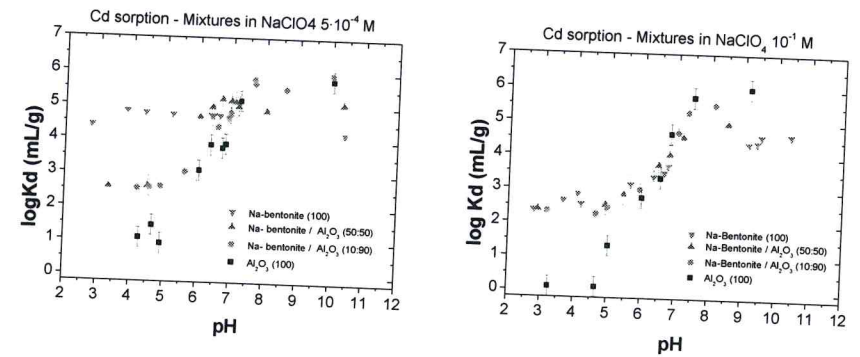
In Na-bentonite /  $\text{Al}_2\text{O}_3$  mixtures particles are fastly coagulated (average size > 1000 nm), even at low ionic strength (Figure 3 Left). This size increment seems to be less effective at alkaline pH, because both Na-bentonite and  $\text{Al}_2\text{O}_3$  are negatively charged and repulsive electrostatic forces may reduce particle interaction. But, the particle destabilisation at low ionic strength and acidic pH is not in agreement to zeta potential measurements (Figure 2).

The charge behaviour of oxides /clay mixtures is complex since oxides and clays exhibit surface charges of different origin. While in bentonite, the structural and pH-independent permanent negative charge is due to isomorphous substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sheets and  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral sheets of the 2:1 layer. The pH-dependent charge on the edges of the lamellar bentonite particles ( $\text{Al-OH}$  and  $\text{Si-OH}$  sites), can be de/protonated.

being positive or negative depending on pH conditions, but this charge is too small to overcome the structural negative charge on the lamellar faces. In oxides, surface sites ( $\text{S-OH}$ ) exhibit different charge depending on pH conditions ( $\text{SOH}_2^+$  for  $\text{pH} < \text{pH}_{\text{IEP}}$  and  $\text{SO}^-$  for  $\text{pH} > \text{pH}_{\text{IEP}}$ ). In the oxide /clay mixtures, complex charge interactions are expected [4, 17, 18].

### Sorption experiments

Figure 3 shows the Cd sorption edges obtained as a function of the pH in  $\text{NaClO}_4$   $5 \cdot 10^{-4}$  M and  $10^{-1}$  M, onto the independent systems and mixtures. In the Figures, two different regions are clearly identified for pH lower or higher than  $\text{pH} \approx 6.5$ .



**Figure 3.** Sorption edges obtained as a function of the pH in  $\text{NaClO}_4$  (Left)  $5 \cdot 10^{-4}$  M and (Right)  $10^{-1}$  M, for Cd sorption onto  $\nabla$  Na-bentonite,  $\blacktriangle$  Na-bentonite /  $\text{Al}_2\text{O}_3$  (50:50),  $\bullet$  Na-bentonite /  $\text{Al}_2\text{O}_3$  (10:90) and  $\blacksquare$   $\text{Al}_2\text{O}_3$  (100) when Cd concentration is kept constant ( $[\text{Cd}] = 4.6 \cdot 10^{-8}$  M).

Cd sorption onto Na-bentonite (100) depends on ionic strength at acidic pH, suggesting a cation exchange process with the aqueous  $\text{Cd}^{2+}$ , as previously described for other bivalent cations [12, 19, 20]. However, the slight dependence on pH observed at the higher ionic strength (Figure 4, right) may indicate the contribution of surface complexation processes.

Cd sorption onto  $\text{Al}_2\text{O}_3$  (100) is independent on ionic strength and highly pH-dependent as expected for an oxide where sorption mainly takes place by surface complexation.

Cd sorption results obtained in the bentonite /  $\text{Al}_2\text{O}_3$  mixtures suggest that at acidic pHs sorption is dominated by Na-bentonite, even though no differences amongst the two studied weight proportions (50:50 or 10:90) are observed. At higher pHs, the addition of  $\text{Al}_2\text{O}_3$  NPs clearly enhances Cd sorption as  $K_d$  values increase with increasing  $\text{Al}_2\text{O}_3$  NPs amount.

At present, modelling of Cd sorption results is in progress in order to verify the hypothesis. Potentiometric titrations were obtained on the independent systems, to obtain the protonation/ deprotonating constants of the surface sites. The hypothesis of Cd cation exchange process onto Na-bentonite is also being verified. Further aim of this experimental study is to

simulate the enhanced Cd sorption behaviour on the Na-bentonite /Al<sub>2</sub>O<sub>3</sub> mixtures, with the thermodynamic constants obtained on the independent systems.

## CONCLUSIONS

The effect of Al<sub>2</sub>O<sub>3</sub> NPs addition on the surface characteristics and sorption properties of Na-bentonite was analysed. Size and zeta potential measurements carried out in the Na-bentonite /Al<sub>2</sub>O<sub>3</sub> mixtures indicated that some particle destabilisation occurred, even at low ionic strength, and this has to be further investigated.

Sorption experiments indicated that the addition of Al<sub>2</sub>O<sub>3</sub> NPs to bentonite, in Al<sub>2</sub>O<sub>3</sub> to bentonite 50/50 and 90/10 ratios, reduces sorption when pH is lower than 6.5 and enhances Cd sorption for pH higher than 6.5, which is shown in the increase of log K<sub>d</sub> value from log K<sub>d</sub> = 4 to log K<sub>d</sub> = 5.5. Modelling of Cd sorption results is in progress, to verify the sorption hypothesis and to demonstrate if enhanced Cd sorption behaviour on the Na-bentonite /Al<sub>2</sub>O<sub>3</sub> mixtures can be described with the thermodynamic constants obtained on the independent systems.

The applicability for other relevant radionuclides, for example with anionic species, should be analysed more in detail.

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