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Effect of γ-radiation on radionuclide retention in compacted bentonite

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ABSTRACT

Compacted bentonite is proposed as an engineered barrier in many concepts for disposal of high level nuclear waste. After the initial deposition however, the bentonite barrier will inevitably be exposed to ionizing radiation (mainly γ) under anoxic conditions. Because of this, the effects of γ-radiation on the apparent diffusivity values and sorption coefficients in bentonite for Cs^+ and Co^{2+} were tested under different experimental conditions. Radiation induced effects on sorption were in general more noticeable for Co^{2+} than for Cs^+, which generally showed no significant differences between irradiated and unirradiated clay samples. For Co^{2+} however, the sorption to irradiated MX80 was significantly lower than to the unirradiated clay samples regardless of the experimental conditions. This implies that γ-radiation may alter the surface characteristics contributing to surface complexation of Co^{2+}. With the experimental conditions used, however, the effect of decreasing sorption was not large enough to be reflected on the obtained D_a values.

1. Introduction

Most concepts for a high level nuclear waste repository (HLNW) involve both natural and engineered barriers in deep geological formations. In a typical HLNW repository such as the Swedish KBS-3 concept, compacted bentonite will be used as a transport barrier for radionuclides (RN) released from the nuclear waste. The rationale for using bentonite is its dense microstructure and swelling capacity in compacted form, rendering diffusion as the only way of transport from or to the canister holding the nuclear waste, as well as the high sorption capacity for many radionuclides. Previous studies have shown that the diffusive transport of radionuclides in water saturated compacted bentonite under ambient conditions is governed by several different parameters, such as compaction, smectite content, ionic strength and the specific interactions between the diffusants and montmorillonite, the main component of bentonite (Eriksen et al., 1999; Kozaki et al., 1998, 2001; Molera and Eriksen, 2002; Van Loon et al., 2007). Under repository conditions however, the bentonite barrier will inevitably be exposed to ionizing radiation (mainly γ from Cs-137) under anoxic conditions. Previous studies concerning γ-irradiation of bentonite with low water contents (Huang and Chen, 2004; Negron et al., 2002; Plötze, 2003; Plötze et al., 2002; Pusch et al., 1993; Pushkareva et al., 2002), have only found small or insignificant effects on both the physical and chemical properties of bentonite and montmorillonite, even at very high doses (several M Gy, 1 Gy = 1 J/kg). However, in two previous studies (Holmboe et al., 2011; Holmboe et al., 2009), radiation induced effects manifested as increased structural Fe(II)/Fe_{Tot} ratio and increased colloid stability, respectively, were found. To the best of our knowledge, no study investigating radionuclide diffusion has yet focused on the effects of ionizing radiation on montmorillonite. In this work we have studied the effects of γ-radiation on sorption and apparent diffusivities in bentonite, under anoxic and oxic conditions. Since diffusion of Co^{2+} and Eu^{3+} through compacted saturated bentonite has been shown to be enhanced in the presence of humics (Wold and Eriksen, 2007) and since native bentonite contains various accessory minerals, both Wyoming Bentonite MX-80 and homo-ionic Na-montmorillonite, with or without addition of humics were probed in the diffusion experiments. In order to specifically study the effect of ionizing radiation on the sorption coefficients, K_d, separate batch sorption experiments were also undertaken.

2. Experimental section

2.1. Materials

The bentonite clay, which was used in this study without further treatment, was the widely studied Wyoming Bentonite MX-80 (MX80) with a montmorillonite content of ~82%. The exchangeable cations for this bentonite are approximately 74.8% Na^+, 16.7% Ca^{2+}, 6.7% Mg^{2+} and 2% K^+. (Karnland et al., 2006). In order to avoid possible effects of the accessory minerals, a purified Na-montmorillonite originating from the montmorillonite reference clay Wyoming

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Montmorillonite Swy-2 (supplied by the Clay Mineral society, hereafter denoted as $SwyNa_w$) was also used in the diffusion experiments. This clay was obtained by (i) Na^+-exchange by repeated washing with 0.5 M Na_2SO_4. (ii) Removal of free iron oxides by a Citrate–Bicarbonate (CB) treatment. (iii) Organic residues and remaining citrate was removed by addition of 2 M H_2O_2 at 70 °C and stirring for 6 h. (iv) Excess carbonates were removed by stirring the suspension at 70 °C at pH 1 after addition of H_2SO_4 for 6 h. Finally the pH of the suspension was neutralized by the addition of small aliquots of NaOH. The remaining dispersion was then dried at 120 °C and grinded to a fine powder. Due to concern with the CB treatment affecting the montmorillonite surface charge and solubility (Stucki et al., 1984) of the $SwyNa_w$ clay experiments, both Na and Ca-montmorillonite originating from Wyoming Bentonite MX-80 were also used, hereafter denoted as WyNa and WyCa, respectively. These clay materials were diluted with 1 M NaCl and left to settle after which the supernatant was removed. The washing procedure was repeated three times after which the clay dispersions were washed and transferred to dialysis membranes and placed in de-ionized water, which was exchanged until the conductivity was below 10 μS/cm. After a final sedimentation step in order to remove the >2 μm fraction, the washing and dialysis cycle was repeated with either 1 M NaCl or $CaCl_2$ after which the clays were dried at 60 °C (Karnland et al., 2006).

The humic substance used in this study was a commercial humic standard (1S102) supplied by the International Humic Substances Society. This humic (HS) was dissolved in NaOH at pH 13 under stirring and neutralized by H_2SO_4 to a pH of ~7.

In order to study the impact of γ-irradiation on weakly sorbing and strongly sorbing tracers in the sorption and diffusion experiments, the radioactive tracers used in this study were $^{137}Cs^+$ and $^{60}Co^{2+}$ (supplied by Isotrak™), respectively, together with 1 μM inactive carrier isotopes.

2.2. Batch sorption experiments

In the batch sorption experiments, samples of 0.090 g clay and a total volume of 18 mL were used to get a volume to mass ratio of 200. In order to qualitatively investigate the effect of γ-radiation to be dependent on water saturation, anoxic/oxic conditions as well as influence of HS, duplicates of different samples were either unirradiated or irradiated with a γ-dose of approx. 60 kGy using a Gammacell 1000 Elite ^{137}Cs-source. All glasswares and equipments used in the experiments were washed in 1% nitric acid prior to the experiments. The samples were either irradiated under inert (N_2) or ambient conditions, either as completely dry or after full water saturation, with or without the presence of 0.1 g/L humic substances in the solutions. Since certain radiation induced effects in the montmorillonite such as changes in the structural Fe(II)/Fe(III) ratio (Holmboe et al., 2011) is oxygen sensitive, one set of samples was kept in a glove box with an oxygen concentration of ~5 ppm. Table 1 summarizes the different combinations of sample setups in the batch sorption experiments. All samples were prepared in duplicates.

Since the sorption of radionuclides is pH dependent, the pH was adjusted to approx. 9 by adding a borate buffer. According to speciation calculations using the software MEDUSA, in combinations with experiments with samples without buffer at the same pH, and the literature, the borate does not affect the system, Table 2. The electrolyte concentration was adjusted to 0.05 M Na_2SO_4, i.e. 0.1 M Na^+, and the radioactive tracers together with an inactive carrier with a concentration of 1 μM were added to all samples. After 5 days of equilibration, the clay suspensions were centrifuged for 30 min at 6000 rpm and the activity in the supernatants was analyzed quantitatively with γ-spectrometry.

Table 1
Summary of the samples in the batch sorption experiments. All samples were prepared in duplicates.

Clay	Atm.	γ-irradiated			Unirradiated	
MX-80	N_2	dry	wet	wet+HS	wet	wet+HS
Na/Ca-Mont	N_2	dry	wet	wet+HS	wet	wet+HS
Na/Ca-Mont	Air	dry	wet	wet+HS	–	–

Table 2
Comparisons of K_d-values for the samples with and without buffer and from the literature.

	Without buffer	With buffer	Molera and Eriksen, 2002
pH	8.9	8.9	9.2
Clay	MX80 unirradiated	MX80 unirradiated	MX80 unirradiated
K_d [cm^3/g]	26 411	12 994	29 178

Two reference samples without clay were prepared with the same procedure as the clay samples and were later used as references in the calculations of the sorbed amount of RN. The dissociation constants, K_d, for each sample were calculated from Eq. 1:

$$K_d = \frac{A_{in} - A_{eq}}{A_{eq}} \times \frac{V}{m} \left[\frac{cm^3}{g}\right] \quad (1)$$

where A_{in} is the activity in the reference sample, A_{eq} is the solution activity at equilibrium, V is the sample volume [cm^3] and m is the mass of the clay in the sample [g].

2.3. Diffusion experiments

In order to have similar montmorillonite density in the diffusion experiment, Bentonite (MX80) and Na-montmorillonite ($SwyNa_w$) were compacted to dry density values of 1.6 and 1.5 g/cm^3, respectively, into diffusion cells made of PEEK (Polyetheretherketone), since this polymer material is known for its high resistance to ionizing radiation. The dimension of the clay plugs, which were confined by two PEEK filters, was 10×5 mm^2 in diameter and length. The diffusion setup is schematically shown in Fig. 1. The different diffusion samples with MX80 and $SwyNa_w$ were generally prepared under same conditions as for the batch sorption experiments, except the diffusion cells samples were saturated and equilibrated with a 0.05 M Na_2SO_4 solution for 6 weeks. Table 1 summarizes the 13 different sample types used in the diffusion experiment. After saturation, the radioactive tracers with 5 μM inactive carrier isotope were added to the inlet solutions. During the diffusion experiment, sampling of the outlet solutions for γ-activity were drawn on a weekly basis during 80 days, after which the experiment was terminated and the clay plugs extruded and sliced into thin sections in order to obtain the tracer concentration profiles within the clay. This was achieved by gravimetric control of each slice and analyzing the activity quantitatively with γ-spectrometry.

3. Results and discussion

3.1. Batch sorption results

The K_d values obtained from the batch sorption experiments for Co^{2+} and Cs^+ with the respective clay material are shown in Figs. 2 and 3, respectively.

The different simulated dashed curves result from a variation in K_d by a factor of 2 from the optimal fit (decreasing in the