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 MGy, $1 \text{ Gy} = 1 \text{ J/kg}$). However, in two previous studies, (Holmboe et al., 2011; Holmboe et al., 2009) radiation induced effects manifested as increased structural $\text{Fe(II)}/\text{Fe}_{\text{Tot}}$ 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 $\sim 82\%$. 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 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 hours. *iv)* Excess carbonates were removed by stirring the suspension at 70 °C at pH 1 after addition of H_2SO_4 for 6 hours. Finally the pH of the suspension was neutralized by 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 where after the supernatant was removed. The washing procedure was repeated three times where after 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 CaCl₂ where after 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 H₂SO₄ 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 ¹³⁷Cs⁺ and ⁶⁰Co²⁺ (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 as 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. 60kGy using a Gammacell 1000 Elite ¹³⁷Cs-source. All glassware and equipment used in the experiments was washed in 1% nitric acid prior the experiments. The samples were either irradiated under inert (N₂) or ambient conditions, either as completely dry or after full water saturation, with or without the presence of 0.1g/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 do not affect the system, Table 2. The electrolyte concentration was adjusted to 0.05 M Na₂SO₄, 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 as analyzed quantitatively with γ-spectrometry.

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 equation 1.

$$K_d = \frac{A_{in} - A_{eq}}{A_{eq}} \cdot \frac{V}{m} \cdot \frac{cm^3}{g} \quad [1]$$

where A_{in} is the activity in the reference sample, A_{eq} is the solution activity at equilibrium, V is the sample volume [cm³] and m is the mass of the clay in the sample [g].

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 due to 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

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/cm³, 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 in diameter and length, respectively. The diffusion setup is schematically shown in figure 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, where after 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.

Figure 1. Illustration of the a) diffusion setup. b) an individual PEEK diffusion cell. c) Photo of the experimental diffusion setup with 16 PEEK cells, kept under N_2 atmosphere in a glove box.

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 Figure 2 and 3 respectively, and tabulated in the supplementary material (Table S.1).

Figure 2. The K_d values for Co^{2+} obtained for the different clay materials, a) MX80 b) WyNa and WyCa and c) SwyNaw.

Figure 3. The K_d values for Cs⁺ obtained for the different clay materials, a) SwyNaw b) WyNa and WyCa and c) MX80.

Figure 4. Typical experimental and simulated diffusion data, here shown for the unirradiator MX80 sample saturated with HS, showing the concentration profiles in the clay plugs of: (a) ⁶⁰Co²⁺, b) ¹³⁷Cs⁺. c) The breakthrough data for ¹³⁷Cs⁺. The different simulated dashed curves results from a variation in K_d by a factor of 2 from the optimal fit (decreasing in the direction of the arrows). Note the insignificant change in a).

For Co^{2+} , the sorption to irradiated MX80 samples not containing HS was significantly lower, approx. 50% of the unirradiated clay samples regardless of the experimental conditions, see Figure 3a. A similar decrease in K_d with approx. 30% was also seen for the MX80 samples subjected to Ca^{2+} addition and the WyCa samples, see Figure 2b. In both the MX80 and the WyCa samples and in the presence of HS, the K_d value of Co^{2+} was further reduced by approx. 70% and irrespective of irradiation, compared to the unirradiated reference sample not containing HS. This effect can be explained by complexation of Co^{2+} to the humic particles, which increase the Co^{2+} concentration out in solution significantly, since the HS was not separated by centrifugation. A similar effect of HS was also seen in the WyNa samples, with the WyNa sample irradiated under anoxic conditions being the exemption. Also for the irradiated WyNa samples without HS, a general decrease of K_d was found, although the K_d values were significantly lower compared to the corresponding MX80 and WyCa samples. This decrease was especially found in the samples irradiated under dry conditions (33%) as well as under wet ambient conditions (25%). However, no detectable effect could be seen between the irradiated and unirradiated sample under anoxic conditions. In the SwyNa_w clay, pretreated with the CB method and H_2O_2 , relatively low K_d values was found compared to the corresponding K_d values obtained with WyNa or MX80, see Figure 2a and 3c, and no significant change due to the different treatments could be found. For Cs^+ , less significant radiation induced effects was found, likely since the clay affinity for Cs^+ is lower than for Co^{2+} . As can be seen in Figure 3a and Figure 3b, with both for MX80 and WyNa, no apparent difference in sorption of Cs^+ was found upon irradiation. However, for the WyCa material, a small decrease in the K_d values for samples irradiated under anoxic conditions was found. Also, addition of HS appeared to bring more Cs^+ out to the solution, significantly decreasing the K_d values, though not to the same extent as with Co^{2+} . As for the samples subjected to a small Ca^{2+} addition, in the MX80 samples and especially in the case of Co^{2+} , the extra addition of Ca^{2+} seemingly reduced the K_d value. This was contrary to the SwyNa_w samples where an increase in K_d upon Ca^{2+} addition was found. The difference between the SwyNa_w clay and the WyNa clay cannot be explained at this moment. However, it is interesting to note that irradiation of WyNa under oxic conditions (see Figure 2b and Figure 3b) as well as treatment with H_2O_2 reduces the sorption capacity of the clays, suggesting that the H_2O_2 impede montmorillonites sorption capacity.

Hence, more obvious radiation induced effects could be found when the K_d of the unirradiated reference was high. This can perhaps be explained by the fact that Co^{2+} sorbs through a close-range surface complexation interaction whereas Cs^+ mainly undergoes sorption through ion-exchange, and competes with the large excess of Na^+ which also may override a small induced radiation effect. Furthermore, a radiation induced decrease of K_d was found in both pre-irradiated and dehydrated samples, as in

saturated samples. This implies that γ -radiation can induce direct effects in the montmorillonite particles.

3.2 Diffusion results

In order to evaluate effects of γ -radiation on Cs^+ and Co^{2+} retention in the compacted and saturated clay materials it was found sufficient to model the apparent diffusivity D_a , qualitatively, using both an analytical method and a numerical method, the latter taking filter effects into account. For the analytical solution, the following equation was used (Crank, 1975) describing diffusion from a 'semi-infinite' source.

$$A_{A_0} = \text{erfc} \frac{x}{2 \sqrt{D_a T}} \quad [2]$$

Furthermore, in order to obtain the apparent diffusivity values and the implicit K_d values from the experimental concentration profiles in the clay plugs as well as from the breakthrough data (Cs^+ only) while at the same time taking the diffusive resistance of the end filters into account, a finite-difference code called ANADIFF was used, see (Eriksen et al., 1999) for details. The water content of all the SwyNa_w and MX80 samples as controlled gravimetrically after termination of the in-diffusion experiment was 1.39 ± 0.05 and 1.64 ± 0.04 g/cm³, respectively. Figure 4 shows typical concentration profiles of Co^{2+} and Cs^+ in the clay plugs together with the corresponding simulated data obtained using the ANADIFF code, see Table 1. The different simulated data, shown as dashed curves shows the effect of K_d values varying by a factor of 2, both increasing and decreasing. Figure 5 shows a comparison between the implicit K_d values for Cs^+ obtained from ANADIFF and the corresponding values obtained in the batch sorption experiment. Since breakthrough of Co^{2+} did not occur during the course of the diffusion experiment, accurate determination of the implicit K_d values for Co^{2+} with ANADIFF was not possible, since the impact of K_d on the concentration profile of Co^{2+} is negligible compared to the D_a . This is illustrated in Figure 4a, with the dashed simulated curves being almost perfectly overlaid showing that the K_d value of Co^{2+} altered by a factor of 2 does not affect the concentration profile in the clay plugs. In the case of Cs^+ , no significant difference between the K_d values as obtained from ANADIFF and batch sorption experiments under different experimental conditions was found, except for the irradiated SwyNa_w samples. This indicates that dispersed HS upon irradiation increases its affinity for Cs^+ , possibly due to degradation to lower molecular residues. On average, the K_d values for the diffusion cell samples were slightly larger than the corresponding batch sorption values, 86 ± 32 cm³/g

Figure 5. The averaged K_d values ($n=2$) for Cs^+ obtained from the ANADIFF simulations (dark grey) compared to K_d values obtained from the batch sorption experiment (light grey).

Figure 6. The D_a values for Cs^+ (top) and Co^{2+} (bottom) obtained in the diffusion experiments, see Table 1. The D_a values are shown for each duplicate as obtained from ANADIFF (dark grey) and the error function, Equation 2 (light grey).

Figure 7. A comparison of hypothetical release through bentonite barrier as a function of K_d with apparent diffusivity values of a) $5 \times 10^{-8} \text{ cm}^2/\text{s}$ and b) $5 \times 10^{-10} \text{ cm}^2/\text{s}$, respectively. The grey squares display the relative RN release vs. K_d after breakthrough (left hand axis) whereas the black circles display the retention time in years before release 1/1000 of the in-diffusing concentration.

and $57 \pm 30 \text{ cm}^3/\text{g}$, respectively. Thus, no apparent difference between the experimental and simulated K_d values was found. The D_a values for both Cs^+ and Co^{2+} obtained from ANADIFF and equation 2 are displayed in Figure 6. As can be seen, the two methods revealed comparable D_a values, and were also found to agree well with diffusion data in the literature (Molera and Eriksen, 2002). In general, the apparent diffusivities of Co^{2+} and Cs^+ were in the same order of magnitude in the irradiated and unirradiated samples (within a factor of 2).

Since the D_a values and overall RN release depend on the amount RN's sorbed in the clay, the impact from an altered K_d values on the RN retention was calculated with ANADIFF. The calculations were performed for a bentonite barrier thickness of 0.35 m and two hypothetical RN's with different D_a values, $5 \times 10^{-8} \text{ cm}^2/\text{s}$ and $5 \times 10^{-10} \text{ cm}^2/\text{s}$, respectively. The resulting RN release is plotted in Figure 7, both in relative terms after breakthrough (left axis) and as the retention time, here defined as the time in years to release 1/1000 of the inlet concentration (right axis). In terms of retention time, the impact of K_d is relatively small. For 'fast' RN's (Figure 7a), having relatively small K_d values ($< 1000 \text{ cm}^3/\text{g}$), the retention time only varies between 21-28 years for K_d values of 100-1000 cm^3/g , i.e. an increase in retention time with 33% by a change in K_d by a factor of 10. For a 'slow' RN (Figure 7b) having a large K_d value, ($> 1000 \text{ cm}^3/\text{g}$) the same relative change is observed for K_d values between 1000-10000 cm^3/g , i.e. varying with a factor of 10, although in absolute numbers the retention time is prolonged with 1000 years. Thus, with decreasing D_a and increasing K_d , the impact of K_d on the retention time before RN breakthrough increases.

Taking the radioactive decay into account, this effect would be even larger. In terms of relative release after breakthrough however, shown on the left hand axis in Figure 7a and Figure 7b as normalized to a K_d value of $50 \text{ cm}^3/\text{g}$, the amount of RN's released, is as expected proportional to the K_d value, i.e. decreasing by a factor of nearly 2 if the K_d value is halved, see also Figure 4c.

Conclusions

The effect on γ -radiation of radionuclide retention and sorption was investigated under different experimental conditions in batch sorption and diffusion experiments. Irradiation of MX80 and WyCa significantly decreased the sorption of Co^{2+} but not Cs^+ . This effect is also seen in the experiments with WyNa, however not from irradiation under anoxic conditions. Thus, depending on the chemical environment, γ -radiation may alter the surface characteristics contributing to surface complexation of Co^{2+} . For Cs^+ , the sorption was found to be comparable in irradiated and unirradiated clays. Hence, more obvious radiation induced effects could be found when the K_d of the unirradiated reference was high. Furthermore, since the radiation induced decrease of K_d was found in both pre-irradiated dehydrated samples as in irradiated saturated samples, the radiation induced decrease of K_d might be caused by direct effects in the montmorillonite particles. Interestingly, irradiation under oxic conditions as well as treating the clay with H_2O_2 decreases the sorption capacity significantly. In the presence of HS, a larger part of Co^{2+} is complexed in the solution phase resulting in lower K_d values towards the clays. On the

contrary, Cs^+ is not affected by the presence of HS, probably since its low affinity to both the HS and clay surfaces anyway. As for the obtained apparent diffusivity values, the effect of decreasing sorption of Co^{2+} to the irradiated clays was unfortunately not large enough to be reflected under these experimental conditions. Furthermore, from ANADIFF simulations of RN transport through a realistic bentonite barrier (thickness 0.35 m), the impact of altered K_d values on the retention time before breakthrough was found to be small in relative terms but large in absolute number of years for slow RN's such as Co^{2+} having low D_a values. In the overall RN release after breakthrough however, the relative amount of released RN was, as expected, found to be proportional to K_d .

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Supplementary material

Table S.1. Summary of the K_d values for Co^{2+} in cm^3/g , obtained from the batch sorption experiment.

	<i>SwyNa_w</i> pH 9	std. dev.	<i>SwyNa_w</i> pH 9 + <i>Ca</i>	std. dev.
γ , dry, N_2	390	40	490	170
γ , dry, Air	440	30	560	40
γ , wet, N_2	410	40	460	50
γ , wet, Air	510	10	610	30
γ , wet, N_2 , HS	280	30	390	80
γ , wet, Air, HS	420	50	530	100
No γ , N_2	350	50	440	90
No γ , N_2 , HS	390	10	560	140

	<i>WyNa</i> pH 9	std. dev.	<i>WyCa</i> pH 9	std. dev.
γ , dry, N_2	950	30	7470	510
γ , dry, Air	970	50	9470	210
γ , wet, N_2	2570	280	7880	960
γ , wet, Air	730	160	9450	1570
γ , wet, N_2 , HS	1960	220	3640	330
γ , wet, Air, HS	630	100	4380	240
No γ , N_2	2800	230	13300	740
No γ , N_2 , HS	980	10	4580	110

	<i>MX80</i> pH 9	std. dev.	<i>MX80</i> pH 9 + <i>Ca</i>	std. dev.
γ , dry, N_2	7130	500	5860	430
γ , wet, N_2	6570	350	5960	450
γ , wet, N_2 , HS	3010	10	2390	150
No γ , N_2	13190	820	9630	1310
No γ , N_2 , HS	3510	770	2580	490