

UNDERSTANDING THE APPARENT DIFFUSIVITY OF SR-85 ION FOR MX-80 IN DIFFERENT SALINITY CONDITION AT LOW DRY DENSITY

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ABSTRACT

The apparent diffusivity of strontium-85 in the compacted MX-80 bentonite under different salinity conditions and dry densities were studied from the viewpoint of activation energy. Through in-diffusions experiments the effect of salinity on diffusion behavior of Sr-85 ions can also be explained. As we know, Sr-90 is by product of the fission materials of nuclear wastes and should be manage properly. Sr-85 is radioactive isotope with the same chemical properties of Sr-90. Adsorption affects only non-steady-state diffusion while at the steady state (e.g., a constant concentration gradient between a constant source and a constant sink), there is no net uptake or release by adsorption, so adsorption has no effect on diffusion (Drever, 1997). The changes in the basal spacing of bentonite as a function of salinity are needed to be observed by the X-ray diffraction method to understand the microstructure changes in diffusion pathways for Sr-85 in MX-80 bentonite. As we know, there could be three potential pathways for radionuclide diffusion in solution-saturated, compacted montmorillonite, i.e., pore water, external surfaces and the internal surface (interlayer spaces) of montmorillonite aggregates. So, it is important to understand the diffusion processes in term of apparent diffusivity of Sr-85 ions in different salinity concentration at low dry density of MX-80. Several parameters are needed in explaining the process such as dry density, activation energy, temperature dependence and concentration of the salinity solutions.

Keywords: Activation energy, apparent diffusivity, different salinity conditions, dry densities, strontium-85

INTRODUCTION

Establishment of criteria for this study was driven from many references including Chuang et al. (2006), Huang et al. (2006) and Risoluti et al. (1999), as well as understanding environmental setting of the study area based on researcher's judgment. Study on the diffusion behavior in the compacted bentonite nowadays is an important issue since it can be used as an engineered barrier system for radioactive waste repository and also as a preparation for nuclear power program in many countries.

An engineered geochemical barrier system consists of various types of elements or minerals in soil which can act as an absorbent for any contamination of radioactive wastes. Diffusivity studies are needed to retard the migration of radionuclide into the groundwater because if there is any leaking, potential to have contamination from drinking water or in many pathways is very high.

MX-80 bentonite from Wyoming State, United States of America contain approximately of 85% of Na/Ca-montmorillonite mineral (di-octahedral smectite) and 15% of accessory minerals (Montes et al., 2005). Montmorillonite clay is known as a candidate buffer material for a safe geological disposal of radioactive waste which can retard radionuclide from migrating away to the groundwater system. It is because of its physical and chemical properties such as swelling properties and low of hydraulic conductivity, low diffusivity and the high sorption capacity of radioactive waste contaminants.

From previous study, the D_a -values for Cs^+ ions is reported to uniformly increased with an increase of ionic strength in both diffusion directions (Sato, 2005). At 298 K, the diffusion coefficients of $^{22}\text{Na}^+$ were found to increase slightly as the NaCl concentrations increased from 0 to 0.5 M (Kozaki et al., 2008). The obtained diffusivities of Sr^{2+} decreased as the density of bentonite increased. The diffusivity for Sr^{2+} varied from 4.3×10^{-7} to 9.0×10^{-8} cm²/s (Molera et al., 2002). Molera also reported that the D_a value of Sr-85 will be increased with the high NaClO_4 concentration from 0.01 M to 0.5 M. The higher the dry density increases the more significant the surface diffusion as compared with the pore diffusion (Lee, 1996). The migration of Sr ions through the compacted bentonite was found to be dominated by surface diffusion (Kim, 1993).

At the room temperature for MX-80 of dry density 1200 and 1800 kg/m³, the apparent diffusion coefficient for strontium ions is about 1.69×10^{-11} and 5.17×10^{-12} m²/s, respectively (Kim et al., 1993). Molera (2002) also reported that the apparent diffusion of strontium ions for MX-80 with the ionic strength of 0.5 M for dry density 1200 and 1800 kg/m³ are 2.5×10^{-11} and 1.2×10^{-11} m²/s, respectively.

Activation energy for diffusion of strontium ions in pure montmorillonite as a function of partial dry density is around 17 kJ/mol at total dry density 1000 and 1200 kg/m³ (Kozaki et al., 1997) and 25.1 kJ/mol at 1700 kg/m³ (Liu et al., 2003). The activation energy for diffusion of sodium ions in compacted montmorillonite at dry density of 1000 kg/m³ as a function of salinity was found to increase from 14 kJ/mol (Kozaki et al., 1998) to 23 kJ/mol for 0 to 0.1 M, and decreased from 23 kJ/mol to 17 kJ/mol when salinity increased from 0.1 M to 0.5 M (Liu et al., 2003).

MATERIALS AND METHODS

Non-steady diffusivity experiments were made in this study for MX-80 bentonite saturated with NaCl solution from different salinity condition of 0 M and 0.5 M NaCl solution. Radionuclide used in this present study was a carrier-free ^{85}Sr (strontium chloride in 0.5 M hydrochloric acid) which was obtained from Japan Radioisotope Association. ^{85}Sr has a half-life of 64.85 days. The small volume of stock solution was diluted by adding small amount of stable carrier SrCl_2 solution to have an appropriate radioactivity before used in the diffusion experiments.

The powdered MX-80 bentonite was compacted in an acrylic resin cell (20 mm in diameters and 20 mm length) to obtain dry densities of 1200 kg/m³ and 1800 kg/m³. In case of dry density of MX-80, the partial montmorillonite dry density in MX-80 has to be considered which is corresponding to the dry density of montmorillonite in Kunipia-F (which is considered as a pure montmorillonite). The samples were dried in a vacuum to make it free from any water before using in the experiments. Water saturation of the compacted montmorillonite has to be allowed in the cells by

contact with deionized water passed through sintered stainless steel filters at room temperature for at least 30 days (Kozaki et al., 2005).

In these diffusion experiments, 1200 kg/m^3 and 1800 kg/m^3 dry densities and four runs having temperatures of 288 – 323 K were made. At different salinity conditions, NaCl concentration varies from 0 M and 0.5 M. A small amount of Sr-85 radiotracer (10 - 20 μl) was spiked to one end of a MX-80 cell-sample. Diffusion of tracer was allowed to proceed by placing two montmorillonite specimens in contact. After prescribed period of time for diffusion, each cell was dissembled and montmorillonite specimens will be sectioned into 05-mm-thick slices as the specimen will be extruded progressively from the cell.

The radioactivity measurements of the Sr-85 tracer were carried out using NaI (sodium iodide) scintillation counter.

RESULTS AND DISCUSSION

Figure 1 shows the typical concentration profiles of $^{85}\text{Sr}^{2+}$ obtained in this study and the effect of diffusion behaviors for the strontium were discussed in the viewpoint of apparent diffusivity and activation energy at different salinity conditions and dry density. The inverse of linear fit concentration of $\ln(C)$ with x^2 was obtained at dry density of 1200 kg/m^3 with the NaCl concentration of 0 M and temperature of 313 K for 72 hours period of time.

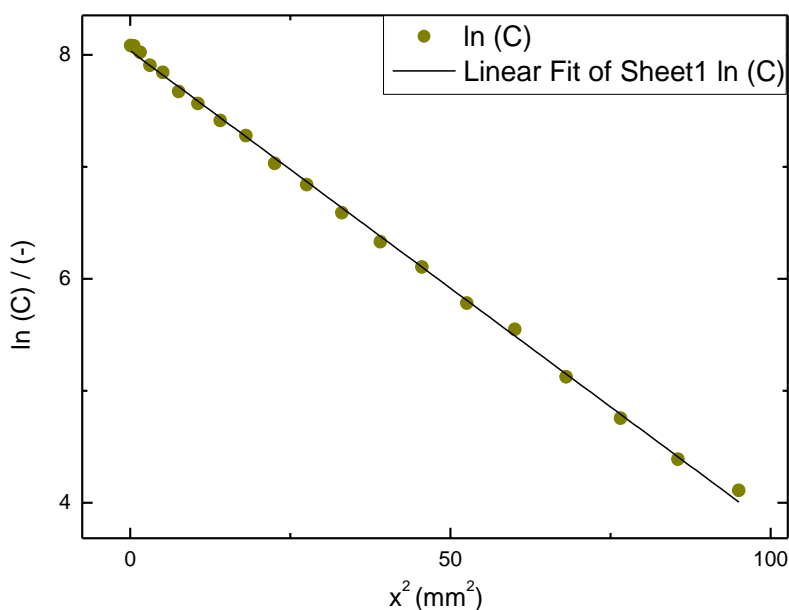


Figure 1: Typical Concentration profile of $^{85}\text{Sr}^{2+}$ ($\rho = 1200 \text{ kg/m}^3$, ionic strength = 0 M, $T = 313 \text{ K}$, $t = 72 \text{ h}$)

Table 1 lists all the D_a values for the compacted MX-80 bentonite which were obtained in the diffusion experiments. At the dry density of 1200 kg/m^3 and 1800 kg/m^3 with the NaCl concentration of 0 M, activation energies of 16.9 and 26.1 kJ/mol respectively were obtained from temperature dependences (288 K – 323 K) of the D_a of strontium ions (Arrhenius plots as shows in

Figure 2) meanwhile 15.3 kJ/mol of the E_a value was obtained at NaCl concentration of 0.5 M at dry density of 1200 kg/m³.

Table 1: Apparent diffusion coefficients of ⁸⁵Sr²⁺ ions in compacted MX-80 bentonite and activation energies for diffusion at a dry density of 1200 kg/m³ (NaCl conc. = 0 M and 0.5 M) and 1800 kg/m³ (NaCl conc. = 0 M)

Cation	Density (Mg m ⁻³)	Ionic strength (M)	Apparent diffusion coefficient [m ² s ⁻¹] (diffusion period of time)				Activation energy, E_a [kJ mol ⁻¹]
			288 K	298 K	313 K	323 K	
Sr ²⁺	1.2	0	1.9 x 10 ⁻¹¹ (96 h)	2.4 x 10 ⁻¹¹ (96 h)	3.8 x 10 ⁻¹¹ (52 h)	4.0 x 10 ⁻¹¹ (48 h)	16.89 ± 1.8
			1.7 x 10 ⁻¹¹ (96.3 h)	2.4 x 10 ⁻¹¹ (96.4 h)	3.1 x 10 ⁻¹¹ (52.5 h)	3.6 x 10 ⁻¹¹ (48.3 h)	
		0.5	3.2 x 10 ⁻¹¹ (49 h)	4.2 x 10 ⁻¹¹ (72 h)	5.3 x 10 ⁻¹¹ (24 h)	6.8 x 10 ⁻¹¹ (20 h)	15.31 ± 1.7
					5.0 x 10 ⁻¹¹ (25 h)		
	1.8	0		1.2 x 10 ⁻¹¹ (312 h)		2.6 x 10 ⁻¹¹ (48 h)	26.14 ± 2.4
				1.1 x 10 ⁻¹¹ (312.5 h)		2.6 x 10 ⁻¹¹ (48.3 h)	

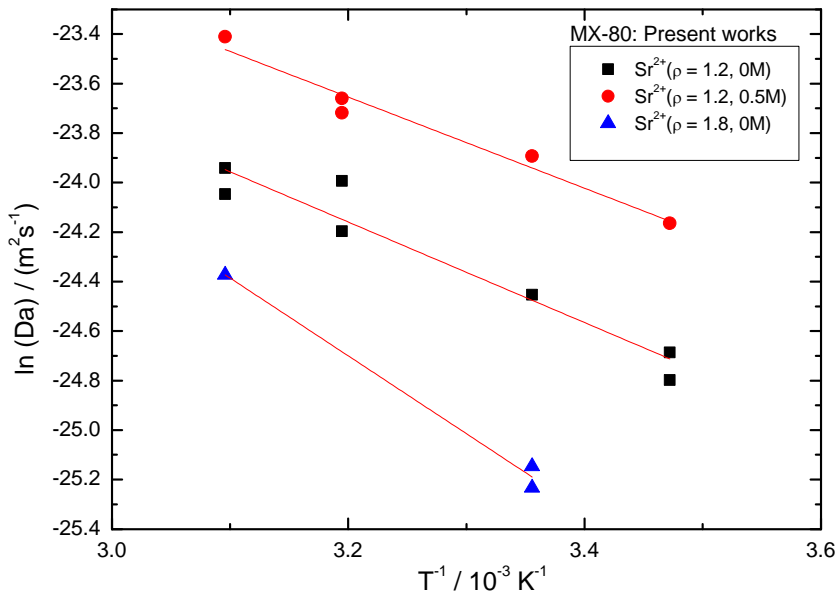


Fig. 2: Arrhenius plots of the Sr²⁺ ions for the MX-80 at different salinity and dry density

It was found that Da slightly increased as the salt concentration increased at dry density of 1200 kg/m³ from 0 to 0.5 M, and decreased at the higher dry density of 1800 kg/m³ (Figure 3). Lower E_a for diffusion were found for MX-80 specimens at lower dry density (1200 kg/m³), while the higher activation energy was at higher dry density (1800 kg/m³) than diffusion of strontium ions in free water, 20.1 kJ/mol (Robinson and Stokes, 1959). At the higher salinity condition for MX-80 at dry density of 1200 kg/m³, the activation energy was found to be constant at NaCl concentrations from 0 to 0.5 M. There was small difference of E_a values for Sr²⁺ which were around 15.3-16.9 kJ/mol (Figure 4).

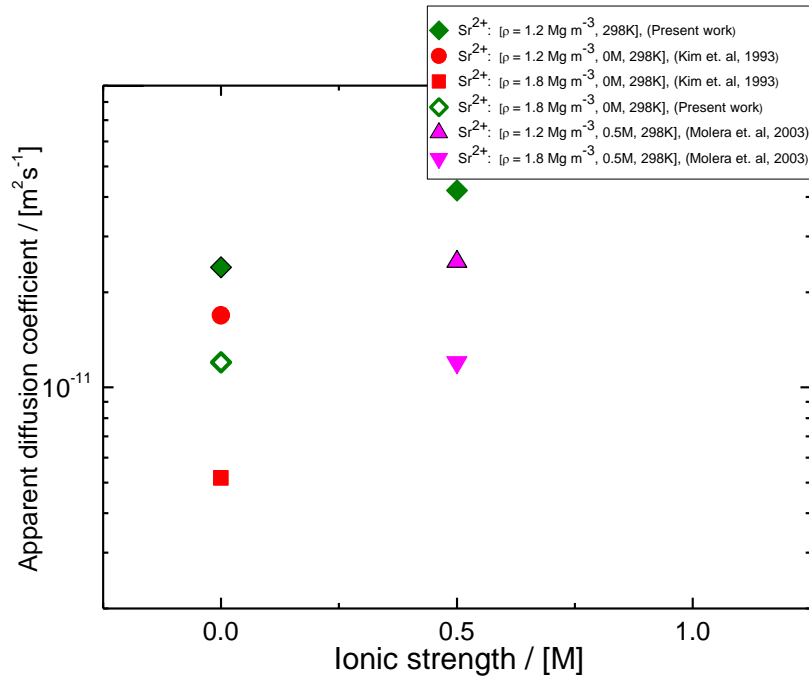


Figure 3: Apparent diffusion as a function of salinity

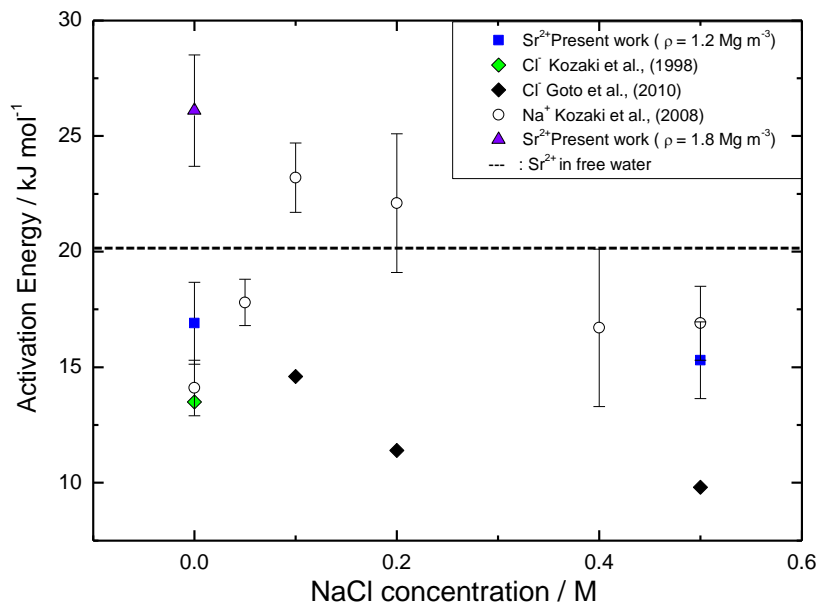


Figure 4: Activation energy as a function of salinity

If the E_a values are constant, Sr²⁺ diffusion could be explained by a single predominant diffusion process such as diffusion in the pore water. However, E_a values obtained in this study were lower than E_a for Sr²⁺ diffusion in free water. This suggests the presence of other diffusion mechanisms than the pore water diffusion. Surface diffusion of the compacted MX-80 which was saturated with distilled water maybe a predominant process for strontium ions at dry density of 1200 kg/m³

because of the existing for electrical double layers (EDL) between the montmorillonite grains. In the Figure 4, the activation energy for the sodium ions at salinity of 0 to 0.1 was found to increase from 14 to 23 kJ/mol and if the changes due to the diminish of EDL and the shrinkage of basal spacing, the interlayer diffusion maybe predominant. As the salinity increased to 0.5 M, the shift of the predominant process for strontium ions in the MX-80 may be changed to the pore water diffusion if we consider the similar trends for sodium ions as shown in Figure 4.

There were some problems arising while conducting the diffusion experiment when the MX-80 cell samples have some corrosion from the stainless steel plates at the water saturation stage. It could change the pH of the water and if it takes more than 30 days water saturated, the water should be changed periodically to avoid the corrosion occurs in the experiments. Some of the cell samples were also found to be broken and cracked and this is probably because of the way of heavy compaction against the cell samples.

CONCLUSIONS

The diffusion processes for the apparent diffusivity of Sr-85 ions of the compacted MX-80 bentonite were studied at the viewpoint of dry density, temperature dependences, activation energy and different salinity conditions. D_a slightly increased as the salt concentration increased at dry density of 1200 kg/m^3 from 0 to 0.5 M, and decreased at the higher dry density of 1800 kg/m^3 . Lower E_a for diffusion were found for MX-80 specimens at lower dry density (1200 kg/m^3), while the higher activation energy was at higher dry density (1800 kg/m^3) than diffusion of strontium ions in free water. At the higher salinity condition for MX-80 at dry density of 1200 kg/m^3 , the activation energy was found to be constant at NaCl concentrations from 0 to 0.5 M. E_a values obtained in this study were lower than E_a for Sr^{2+} diffusion in free water that suggests the presence of other diffusion mechanisms than pore water diffusion in this study. There is more than one pathway in diffusion processes to explain the diffusivity behavior of the strontium ions in the MX-80 compacted bentonite.

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