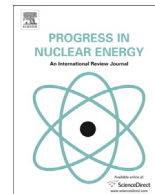




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## Diffusion and adsorption of uranyl ion in clays: Molecular dynamics study

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### ABSTRACT

Molecular dynamics (MD) simulations were performed to study the diffusion and adsorption behaviors of aqueous uranyl species in interlayer space of clay minerals, which are key processes in the safety assessment for geological disposal of radioactive waste. The diffusion behaviors of  $\text{UO}_2^{2+}$ ,  $\text{K}^+$ ,  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  were evaluated for the aqueous solution system. The diffusion coefficients of these species decreased with increasing solutes concentration, and that of  $\text{UO}_2^{2+}$  was much smaller than others. In the aqueous solution with higher concentration of carbonate ions, uranyl carbonate complexes such as  $\text{UO}_2\text{CO}_3$  and  $\text{UO}_2(\text{CO}_3)_2^{2-}$  could be observed. For the clay-aqueous solution system (clay: montmorillonite or illite), the adsorption and diffusion behaviors of  $\text{UO}_2^{2+}$  and  $\text{K}^+$  were evaluated by MD calculations. The distribution coefficients ( $K_D$ ) of these solutes increased with the layer charge of clay, and the  $K_D$  value of  $\text{UO}_2^{2+}$  might be smaller than that of  $\text{K}^+$ . Further, the diffusion coefficients in the adsorption layer on the basal plane were relatively small and decreased with increasing the layer charge of clay.

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### 1. Introduction

Compacted bentonites and argillaceous rocks are widely considered in many countries as suitable barrier materials for the safe geological disposal of radioactive waste (NEA, 2012). The suitability of these materials arises from its high clay (such as montmorillonite and illite) contents, which has a large surface area with abundant reactive sites. In order to evaluate the long-term performance of these barrier materials, it is necessary to understand and quantify the diffusion and adsorption processes of radionuclides in these materials and to develop predictive models that can be applied under the expected environmental conditions of geological disposal. Various types of quantitative modeling approaches in these materials have been developed for both diffusion and adsorption [e.g. (Bourg et al., 2006; Appelo et al., 2010; Tachi and Yotsuji, 2014)]. In addition, molecular dynamics (MD)

simulations have been recently applied to predict the diffusivities of water and simple cations in montmorillonite interlayers [e.g. (Rotenberg et al., 2007; Bourg and Sposito, 2010)]. However, these models and simulation have focused mainly on water and simple ions, whereas those related to more complex actinides are few [e.g. (Tachi et al., 2010, 2014a, 2014b; Greathouse and Cygan, 2005; Liu et al., 2013)]. In the context of radioactive waste disposal, important challenges are extending the applicability of such models and simulations to radionuclides with a complex aqueous chemistry, especially actinides.

Uranium (U) is one of the most considerable actinides for the radioactive waste disposal, and uranyl ( $\text{UO}_2^{2+}$ ) ion is the major chemical species to stably exist in the wide pH and Eh ranges (Runde et al., 2002; Choppin, 2006; Krestou and Panias, 2004). In the presence of carbonate as a common ligand in groundwater, aqueous uranyl carbonate complexes,  $\text{UO}_2(\text{CO}_3)_x^{2(x-1)-} \cdot n\text{H}_2\text{O}$ , are found to be the major chemical species (Hu et al., 2008; Allard et al., 1984; Murphy et al., 1999). Under the slightly oxidizing condition and the mild reducing condition with  $\text{CO}_3^{2-}$  ions,  $\text{UO}_2^{2+}$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$  are dominating soluble species at  $\text{pH} < \sim 7$ ,

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**Table 1**  
Potential parameters of water, clay and soluble species.

Atom	$z$ ( $e$ )	$a$ [Å]	$b$ [Å]	$c$ [(kcal mol <sup>-1</sup> ) <sup>1/2</sup> Å <sup>3</sup> ]			
Water(w)							
O	-0.92	1.728	0.1275	27.74			
H	0.46	0.035	0.044	–			
Clay							
O	-1.1 to -1.2 <sup>a</sup>	1.868	0.151	27.00			
Si	2.10	0.987	0.083	0.0			
Al	1.95	1.089	0.088	0.0			
Mg	1.52	1.137	0.101	2.0			
H	0.46	0.074	0.032	0.0			
Solute ion							
Na	1.00	1.314	0.115	8.0			
K	1.00	1.546	0.115	14.0			
Cl	-1.0	2.061	0.190	28.0			
Two body terms for covalent bond							
	$D_1$ [kcal mol <sup>-1</sup> ]	$\beta_1$ [Å <sup>-1</sup> ]	$D_2$ [kcal mol <sup>-1</sup> ]	$\beta_2$ [Å <sup>-1</sup> ]	$D_3$ [kcal mol <sup>-1</sup> ]	$\beta_3$ [Å <sup>-2</sup> ]	$r_3$ [Å]
O <sub>w</sub> -H <sub>w</sub>	13711	7.4	-523	3.13	8.3	12.8	1.283
O-Si	49200.0	5.0	-3281.0	2.24	0.0	0.0	0.0
O-Al	36200.0	5.0	-1936.0	2.24	0.0	0.0	0.0
Three body terms for covalent bond							
	$f$ [10 <sup>-11</sup> J]	$\theta$ [degree]	$r_m$ [Å]	$g_r$ [Å <sup>-1</sup> ]			
H <sub>w</sub> -O <sub>w</sub> -H <sub>w</sub>	0.000115	99.5	1.43	9.2			
Si-O-Si	0.000061	120.0	1.77	16.8			

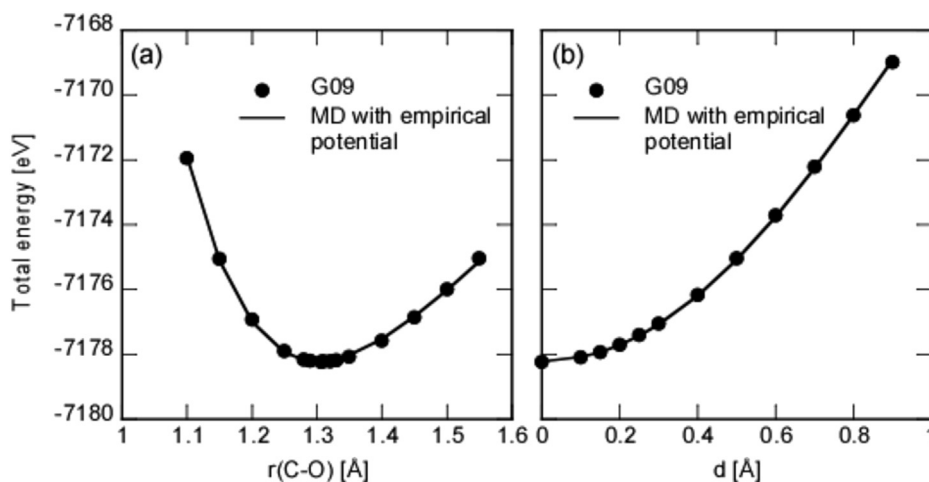
<sup>a</sup> Partial charge of oxygen ion depends on the chemical composition of clay.

6 < pH < 10 and pH > 8, respectively (Choppin, 2006; Krestou and Panias, 2004; Hu et al., 2008; Allard et al., 1984). Speciation and diffusion behavior of UO<sub>2</sub><sup>2+</sup> with or without CO<sub>3</sub><sup>2-</sup> ions in the aqueous solutions already were evaluated by classical molecular dynamics (MD) simulations (Kerisit and Liu, 2010). Kerisit and Liu showed that the diffusion coefficient of uranyl carbonate complex decreased with an increase of its size in the aqueous solution (Kerisit and Liu, 2010). From the technical viewpoint of MD simulations, the interatomic potential function based on the AMBER force field was often used for UO<sub>2</sub><sup>2+</sup> ion in the previous MD studies (Guilbaud and Wipff, 1993, 1996; Pearlman et al., 1995). On the other hand, some potential functions, e.g. TIP3P, SPC/E, SPE, were proposed as the force field of water molecule and their validity was assessed (Berendsen et al., 1987; Jorgensen et al., 1983). In addition,

the potential models of CO<sub>3</sub><sup>2-</sup> ion were obtained in accordance with the potential functions of H<sub>2</sub>O and UO<sub>2</sub><sup>2+</sup> molecules (Kerisit and Liu, 2010).

Montmorillonite and illite that are key components in barrier materials and have almost the same crystal structure constructed by the repetition of T-O-T layers (T: Tetrahedron, O: Octahedron). The simplest composition of montmorillonite, for instance, can be expressed in Na<sub>x</sub>(Al<sub>2-x</sub>Mg<sub>x</sub>)Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·nH<sub>2</sub>O ( $x \sim 0.2-0.6$ ) and that of illite is K<sub>x</sub>Al<sub>2</sub>(Si<sub>4-x</sub>Al<sub>x</sub>)O<sub>10</sub>(OH)<sub>2</sub>·nH<sub>2</sub>O ( $x \sim 0.5-1.0$ ). Here, the tetrahedron in the T-O-T layer consists mainly of Si and four O ions, and the octahedron consists mainly of Al and six O ions. The isomorphous substitution between Al and Mg ions occurs on octahedral sites in montmorillonite, and that between Si and Al ions occurs on tetrahedral sites in illite, which results in the negative layer charge of clays. Therefore, the positive exchangeable ions exist with water molecules in the interlayer spaces between the T-O-T layers in order to keep the electrical neutrality. For above compositions of clays, Na<sup>+</sup> and K<sup>+</sup> ions correspond to the exchangeable ones in montmorillonite and illite, respectively. A part of the positive exchangeable ions is attracted by adsorption sites, e.g. basal planes and edges, and moves around in the interlayer spaces and pores in clays. An interaction between UO<sub>2</sub><sup>2+</sup> ion and clay mineral has been analyzed for the system coexisting with water molecules by MD simulations (Greathouse and Cygan, 2005, 2006). Quarts, beidellite, montmorillonite and etc. were picked up in previous studies (Greathouse and Cygan, 2005, 2006; Greathouse et al., 2002), and the CLAYFF potential model was used to simulate the system including those clay minerals (Greathouse and Cygan, 2005; Liu et al., 2013; Cygan et al., 2004).

The purpose of this study is to systematically evaluate the diffusion and adsorption behaviors of soluble actinide species in clays relevant to geological disposal of radioactive waste. As a first step for the molecular modeling of the above system, the interaction potential models of UO<sub>2</sub><sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> were newly constructed based on the free flexible force field model proposed by Kawamura (Suzuki and Kawamura, 2004; Kawamura, 2008), and MD calculations were performed for the aqueous solution system and the clay-aqueous solution system where clays: montmorillonite and illite to focus on their layer charge and structure. In the following sections, the simulation details, the diffusion and the adsorption behaviors of soluble species in the aqueous system with or without clay minerals are presented.



**Fig. 1.** Total energies of CO<sub>3</sub><sup>2-</sup> as a function of the distance between C and O (a) and as a function of the distance between C and the plane constructed by three O atoms (b). Data expressed in solid circle and line were calculated by Gaussian09 (G09) and MD, respectively.

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