

A DFT study of the Radium Adsorption on Bentonite

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1. Introduction

Radium is a naturally occurring radioactive material (NORM), but it is also produced through the radioactive decay of uranium in spent nuclear fuel. In the Swedish safety scenario[1], radium was estimated to be the largest contributor to an effective dose in the event of a canister breakage and subsequent release of radionuclides into the buffer material and surrounding environments. The migration of radium from spent nuclear fuel into the environment is predominantly governed by surface interactions through an adsorption mechanism. Several studies[2-4] have investigated the behavior of Ra(II) in the environment using experimental and theoretical methods. However, previous studies have not been extended to the behavior of radium in the bentonite. Therefore, this investigation elucidates the adsorption characteristics of radium on the bentonite surface through Density Functional Theory (DFT) calculations.

2. Computational Approach

2.1 Computational details

Here, ab initio DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) version 6.3.0. The generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE-GGA) was used for exchange–correlation energy for all elements. The cut-off energy was set as 400 eV and 600 eV for geometry optimization and self-consistent field calculation, respectively. The Brillouin zone was sampled using a Monkhorst-Pack ($6 \times 4 \times 3$) grid for the bulk model. The slab models were calculated using a ($3 \times 4 \times 1$) Monkhorst-Pack grid. A vacuum region of 15 Å was applied along the z-axis to avoid vertical interactions.

Initial atomic coordinates were derived from the bentonite structure from the American Mineralogist Crystal Structure Database. The optimized cell parameters for bentonite were determined as follows: $a = 5.03$ Å, $b = 8.68$ Å, $c = 9.81$ Å, $\alpha = 90.00^\circ$, $\beta = 98.55^\circ$, $\gamma = 90.00^\circ$, with the unit cell formula of $\text{Na}_2\text{Al}_4\text{Mg}_2\text{Si}_8\text{O}_{24}$.

2.2 Adsorption energy

The adsorption energy (ΔE_{ads}) was calculated as

$$\Delta E_{\text{ads}} = \Delta E_{\text{total}} - (\Delta E_{\text{slab}} + \Delta E_{\text{Ra-complex}}) \dots (1)$$

where E_{total} is the total energy of the system after the adsorption reaction, E_{slab} is the total energy of the bentonite slab and $E_{\text{Ra-complex}}$ is the total energy of an isolated radium complex. Negative adsorption energy suggests that the formation of the complex is energetically favorable.

3. Results and discussion

3.1 Hydrated and hydroxyl-hydrated Ra system

In this paper, we performed DFT optimization for the hydration system of Ra, considering the number of water molecules and the presence of hydroxyl groups. As the coordination number increases, the Ra-O_w bond length increases subtly and the formation energy decreases simultaneously, indicating improved stability. Therefore, $[\text{Ra}(\text{H}_2\text{O})_8]^{2+}$ is considered the most stable structure for hydrated Ra²⁺ ions in solution. We substituted the water molecules in the hydrated complex with two hydroxyl groups to obtain $(\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_{n-2})$. This finding suggested that $[\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_4]$ is recognized as the most stable configuration of the hydroxyl-hydration system. These two complexes are used as initial configurations for bentonite surface adsorption and are shown in Figure 1.

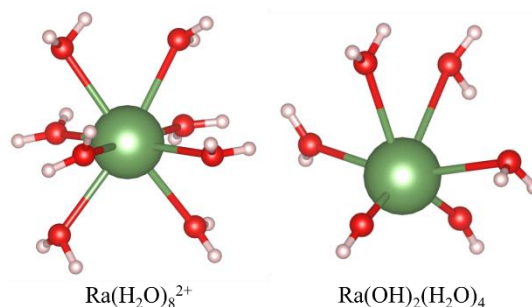


Figure 1. The equilibrium geometries of the hydrated system, $\text{Ra}(\text{H}_2\text{O})_8^{2+}$ and the hydroxyl-hydrated system, $\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_4$.

3.2 Adsorption of Ra complexes on bentonite

The hydrated and hydroxyl-hydrated Ra adsorption on bentonite (001) and (010) facets were calculated. The equilibrium adsorption geometry of $\text{Ra}(\text{H}_2\text{O})_8^{2+}$ on bentonite (001) facets was found to be the outer-sphere configuration. In the $\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_4$ system, the two hydroxyl groups interact with reactive surface oxygen to form an inner-sphere complex with radium.

The (010) facet of bentonite exhibits stronger activity than the (001) facet due to the presence of hydroxyl groups[5]. The equilibrium geometry of the adsorption on the (010) facet shows the formation of hydrogen bonds between the hydroxyl groups on the Mg-OH surface and the H_2O in the hydrated radium. In the $\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_4$ system, the hydroxyl-hydrated radium reacts with the hydroxyl group of Mg-OH and one of the hydrogens of Si-OH dissociates and attaches to the hydroxyl group of radium to form a water molecule. Their adsorption energies, E_{ads} were summarized in Table 1. It was clearly shown that the E_{ads} value on (010) was much lower than on (001) in both radium systems, suggesting more favorable Ra adsorption on the (010) facet.

Table 1. The adsorption energies of $\text{Ra}(\text{H}_2\text{O})_8^{2+}$ and $\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_4$ on bentonite surfaces (kcal/mol).

	On (001) facet	On (010) facet
$\text{Ra}(\text{H}_2\text{O})_8^{2+}$	-56.362	-162.539
$\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_4$	-101.405	-141.398

4. Conclusions

This study investigates the adsorption mechanisms of $\text{Ra}(\text{H}_2\text{O})_8^{2+}$ and $\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_4$ species, two major Ra species in solution on the bentonite surface using the plane-wave pseudopotential DFT method. Hydrated $\text{Ra}(\text{H}_2\text{O})_8^{2+}$ exhibits outer sphere configurations on two bentonite facets. Hydroxyl-hydrated $\text{Ra}(\text{OH})_2(\text{H}_2\text{O})_4$ formed the inner sphere complexations with two facets of bentonite. Based on the adsorption energies, outer-sphere adsorption of hydrated $\text{Ra}(\text{H}_2\text{O})_8^{2+}$ on the deprotonated hydroxyl group of the bentonite (010) surface is suggested as the main adsorption mechanism. Our results provide a deeper insight into the behavior of radium in buffer materials.

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