Integrated DFT and Experimental Studies of Radium Adsorption on Buffer Materials

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Keywords: Adsorption, Buffer materials, Montmorillonite, Spent Nuclear fuel, Radium, Barium

1. Introduction

Radium (Ra) is a naturally occurring radioactive material that primarily exists as Ra^{2+} in the Earth's crust and exhibits chemical behavior similar to that of barium (Ba). Among its isotopes, ^{226}Ra is of particular concern due to its long half-life and radiological hazards and is recognized as a major contributor to long-term radiation dose following canister corrosion in deep geological repositories[1]. Bentonite, specifically consisting of montmorillonite (MMT), is widely used as a buffer material in engineered barrier systems to effectively retard Ra migration into the biosphere. In this study, we integrate density functional theory (DFT) calculations with batch adsorption experiments to systematically investigate stable Ra adsorption configurations on distinct MMT facets. This combined theoretical and experimental approach provides deeper insight into Ra interactions with buffer materials and improved long-term safety assessments for deep geological repositories.

2. Methods and Results

2.1 Computational details

DFT calculations were conducted using Vienna Ab initio Simulation Package (VASP) 6.3.0, employing the Perdew-Burke-Ernzerhof functional[2], and the DFT-D3 method accounts for van der Waals corrections. Two MMT facets were examined: the permanently negatively charged (001) basal facet and the hydroxyl-rich, pH-dependent (010) edge facet. The optimized lattice parameters showed good agreement with experimental values. A vacuum spacing of 15 Å was introduced in the slab models to eliminate vertical interactions. Hydrated and hydroxyl-hydrated Ra species were modeled based on previous EXAFS analyses[3] as $[Ra(H_2O)_n]^{2+}$ and $Ra(OH)_2(H_2O)_{n-2}$. Identical hydration models were applied to Ba, allowing a direct comparison of their adsorption behaviors.

2.2 Experimental method and materials

Batch experiments were performed using WRK bentonil, pretreated by exchanging interlayer cations with Na^+ using a 1 M $NaNO_3$ solution. The radioisotope ^{226}Ra was used for adsorption isotherm and pH-dependent experiments. The radioactivity of ^{226}Ra was measured using liquid scintillation counting (LSC-5110TR), with analysis performed after 21 days to ensure secular equilibrium with its daughter nuclides. In addition, Ba was used as a non-radioactive surrogate to conduct additional experiments on adsorption isotherm, kinetics, pH-dependent, and ionic strength-dependent experiments. Ba concentrations were measured using inductively coupled plasma mass spectrometry (ICP-MS).

2.3 Results and Discussion

This study identified the three dominant aqueous complexes of Ra and Ba by evaluating variations in hydration and hydroxyl coordination. As shown in Figure 1, $Ra(OH)_2(H_2O)_4$ preferentially forms stable inner-sphere complexes on the (001) facet, while both Ra^{2+} and $Ra(OH)_2(H_2O)_4$ exhibit outer-sphere adsorption with hydrogen bonding on the (001) facets. However, on the (001) facet, $Ra(OH)_2(H_2O)_4$ exhibits lower adsorption energy than $Ba(OH)_2(H_2O)_4$, likely due to differences in hydration energy.

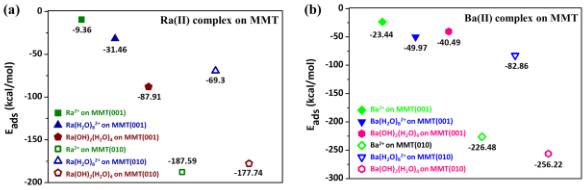

Figure 1. Comparison of adsorption energies of (a) Ra- (b) Ba-complexes adsorbed on both MMT facets

Furthermore, we investigated the effect of pH on the adsorption behavior of Ra and Ba at the hydroxyl-rich (010) facet. Across a broad pH range, Ba consistently exhibited lower adsorption energies than Ra, suggesting stronger surface interactions. At high pH, both Ra and Ba showed increased adsorption affinity for the (010) facet.

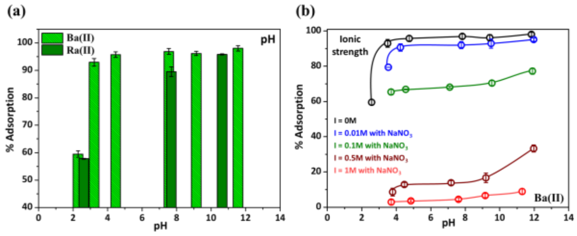

Figure 2. Effect of (a) pH on Ra and Ba adsorption and (b) ionic strength on Ba adsorption in batch experiments.

Batch adsorption experiments confirmed that Ra follows a linear isotherm and exhibits the highest uptake under high pH conditions(see Figure 2(a)). Notably, Figure 2(b) shows a sharp decrease in Ba adsorption with increasing ionic strength, suggesting that Ba primarily forms outer-sphere complexes with MMT. This interpretation is further supported by the fact that the (010) facet—where inner-sphere complexation is more likely—constitutes only about 10% of the total MMT surface area. However, the observed increase in adsorption at high pH indicates that the hydroxyl-rich (010) facet still plays a meaningful role. As the pH rises, the deprotonation of surface hydroxyl groups enhances their reactivity, promoting inner-sphere complexation. This suggests that while outer-sphere complexation dominates, inner-sphere complexation at the (010) facet becomes increasingly relevant at elevated pH. These findings enhance our understanding of Ra and Ba retention in bentonite, which is essential for optimizing buffer materials design in deep geological repositories.

3. Conclusions

This study employed DFT calculations and batch adsorption experiments to investigate the adsorption behavior of radium (Ra) on montmorillonite (MMT), the primary component of bentonite used in buffer materials for deep geological repositories.

Theoretical and experimental results demonstrated that Ra adsorption is enhanced at high pH conditions, with $Ra(OH)_2(H_2O)_4$ forming stable inner-sphere complexes on (010) facets. Ba exhibited a stronger affinity for the (010) facet over a broad pH range, while Ra showed greater stability on the (001) facet, likely due to differences in hydration energy.

Batch adsorption experiments confirmed that Ra adsorption follows a linear isotherm, with its behavior significantly influenced by varying pH. In addition, Ba adsorption experiments offered additional insight into isotherm behavior, kinetics, and ionic strength effects, highlighting the MMT surface interactions of alkaline earth metals. The ionic strength-dependent decrease in Ba adsorption indicates predominant outer-sphere complexation, yet increased uptake at high pH suggests that the (010) facet still contributes through inner-sphere complexation under alkaline conditions.

These findings provide insight into the interactions of Ra and Ba surfaces with MMT and highlight the importance of mineral surfaces and geochemical conditions in radionuclide retardation. This study supports the design of buffer materials within effective engineered barrier systems and contributes to improving the long-term safety of deep geological repositories.

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Acknowledgment

This work was supported by the Institute for Korea Spent Nuclear Fuel (iKSNF) and National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science and ICT, MSIT) (No.2021M2E1A1085203).