

Molecular simulation of competing sorption of U(VI) on the surface of clay and mineral wastes

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Abstract. *In-situ* uranium extraction technology, nuclear fuel processing, water purification require detailed study of sorption process of U(VI) and some compete coexisting ions onto clay and waste materials. The Monte-Carlo method used for modeling of the U(VI), Al(III), Fe(II)/Fe(III) sorption on the surface of the clay materials (vermiculite, kaolinite, illite, palygorskite, biotite, montmorillonite, nontronite) and mineral wastes (zincite, franklinite) which are capable to effective sorption of U(VI) on the mineral surfaces. The molecular modeling used different species (UO_2^{2+} , UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, AlSO_4^+ , $\text{Al}(\text{SO}_4)_2^-$, FeSO_4^-) in acidic sulfate solutions (H_2SO_4 , HSO_4^- , SO_4^{2-}). Different sorption energy values indicate chemical nature of the adsorption process with predominant sorption of uranium ions (UO_2^{2+} and $\text{UO}_2(\text{SO}_4)_2^{2-}$) compared with Fe/Al ion species.

1 Introduction

The process of the uranium U(VI) sorption on clay materials is an important in nuclear power engineering, water purification and a number of applications related to radionuclide treatment. It is known that clay materials can be effective sorbents for uranium due to various surface functional groups. The uranium sorption involves a number of interactions between clay surface and ions through different mechanisms, such as ion exchange, adsorption and metal complex coordination mode. There are many important factors influencing the efficiency of uranium extraction in nature as well as *in-situ* leaching technology (pH, uranium concentration in solution, morphology/structure of clay materials, and etc.). The attempts of adjusting these parameters can improve the uranium extraction. Study of the U(VI) sorption on clay sorption materials is carried out to develop new effective and environmentally friendly methods for uranium extraction from wastewater or technological solutions in hydrometallurgy [1].

The *in-situ* process of uranium leaching combined with the process of partial sorption of uranium on the surface of bentonite minerals on the boundary surface and clay minerals of

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the sandy ore horizon. The UO_2^{2+} forms sulfate complex compounds in acidic aqueous solution. Thermodynamically, several different species with different charges are possible in sulfuric acid solutions ($\text{UO}_2\text{SO}_4(\text{aq})$, $\text{UO}_2(\text{SO}_4)_2^{2-}$ and $\text{UO}_2(\text{SO}_4)_3^{4-}$) [2]. At $\text{pH} > 5$, various sulfate complexes with a bridging hydroxide ion, as well as, oxide forms are possible in solutions [1-3]. Moreover, sulfate ions have ability to form mono- and bidentate sulfate complexes. The presence of monodentate coordination was confirmed using high-energy X-ray scattering (HES) in equimolar solutions of $[\text{SO}_4^{2-}]_{\text{tot}}/\text{U}(\text{VI})$ [2] and correlated with data obtained using FTIR and Raman spectra. However, data from extended X-ray absorption fine structure spectroscopy (EXAFS) indicate bidentate coordination at high concentrations of sulfate ions in solution [4].

The purpose of this work is Monte Carlo simulation of adsorption of U(VI) particles on the surfaces of the clay (kaolinite, illite, palygorskite, biotite, vermiculite, montmorillonite, nontronite) and waste (zincite, franklinite) mineral materials.

The relevance of this study related to advanced research in field of effective adsorbents and computer modelling which are driving forces for molecular understanding of the complicated processes under current experimental approaches. Among various computational methodologies, molecular dynamics, density functional theory, Monte Carlo method have been widely used to match and justify experimental observations by unique information at atomic-scale and femtosecond time [5,6].

2 Experimental part

The species distribution of *in-situ* solutions was calculated by MINTEQ software using experimental data of *in-situ* uranium extraction solutions in sulfuric acid (Table 1).

Table 1. Chemical composition of *in-situ* uranium extraction solutions.

Composition	pH	SO_4^{2-}	U	Fe^{3+}	Fe^{2+}	Al^{3+}
Concentration, mg/l	1.2	12750	40.4	730	240	544

The Monte Carlo (MC) method simulated the sorption of uranium, iron and aluminium ions from sulfate aqueous solutions. Full simulation of the MC atomic force field to study competitive interaction mechanism of various forms of U(VI), Al(III), Fe(II)/Fe(III) in solution on the surface of clay adsorbents in aqueous sulfuric solution with excess of sulfate ions (H_2SO_4 , HSO_4^- , SO_4^{2-}) was carried out using the “Forcite” and “Adsorption Locator” modules in the BIOVIA Accelrys Material Studio 2017 software package.

To create a simulated sorbate/sorbent system, data from cif-files (Crystallography Open Database) for kaolinite (9009234), montmorillonite (9002779), biotite (1524087), vermiculite (1001031), illite (2300189), palygorskite (9010433), nontronite (9010766), zincite (1011258) and franklinite (9005110) were used. The predominant crystalline surfaces of clay and waste materials determined by X-ray diffraction (XRD) using a number of reflections with maximum intensities from corresponded crystalline planes in XRD pattern (Figure 1).

Water molecules and a set of modelled ions were placed inside the simulation supercells with dimensions ($31\text{\AA} \times 55\text{\AA} \times 118\text{\AA}$) under periodic boundary conditions. The complete modeling procedure used an appropriate force field to optimize the structures of all sorbate molecule and ion species (sorbent/ sorbate /water). In order to simulate a real *in-situ* environment, up to 150 molecules of water, sulfate ions were added to supercell, and the surface of the clay sorption material was protonated to take into account the acidic nature of *in-situ* production solutions.

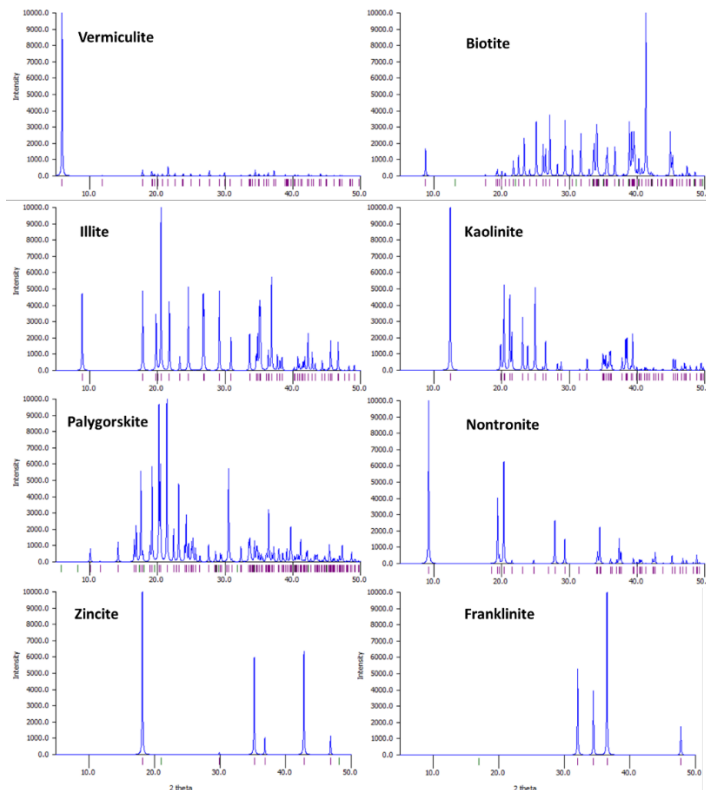


Fig. 1. XRD patterns used in MC simulations.

3 Results and discussions

3.1 Monte Carlo simulation of U(VI) sorption in H₂SO₄ solutions

The MC modeling study purpose is determination of a number of low-energy adsorption sites to study most preferential localization of various sorbate particles on the surface of the clay and waste materials. It should be useful to find the relationship between the mineral nature and the mineral adsorption capacity as an initial approximation. The MC simulation is an effective method to understand adsorption mechanism and predict the adsorption energy (E_{ads}). The surface of various clay sorption materials can sorb different species of U(VI), Al(III), Fe(II)/Fe(III) in an acidic sulfuric acid solution (pH = 1.2) (Table 2).

Indeed, experimental studies confirmed formation of U(VI) outer-sphere complexes on bentonite clays at low pH and ionic strength, as well as inner-sphere complexes related to pH and ionic strength. The graphical distribution of calculated ion species (Figure 2) indicates most predominate ions in sulfuric acid solutions at pH=1,2 (UO_2^{2+} , UO_2SO_4 , $UO_2(SO_4)_2^{2-}$, $AlSO_4^+$, $Al(SO_4)_2^-$, $FeSO_4^-$, H_2SO_4 , HSO_4^- , SO_4^{2-}). These sets of species applied for MC simulations of sorption on the protonated surface of different types of clay and waste materials (kaolinite, illite, palygorskite, biotite, vermiculite, montmorillonite, nontronite, zincite, franklinite). The MC method allows show possible correlation between adsorption energies for various clay and waste materials in comparison with previously obtained experimental data on U(VI) sorption [1,2]. The adsorption energy values (E_{ads}) were

calculated based on the average adsorption energy of the different equilibrium configurations (Table 3).

Table 2. Calculated species distribution at pH=1,2 of in-situ uranium extraction sulfuric solution.

Component	% of total concentration	Species name
Sorbate species (single)		
UO ₂ ²⁺	17.635	UO ₂ ²⁺
	65.452	UO ₂ SO ₄ (aq)
	16.913	UO ₂ (SO ₄) ₂ ²⁻
SO ₄ ²⁻	19.204	SO ₄ ²⁻
	0.075	UO ₂ SO ₄ (aq)
	0.039	UO ₂ (SO ₄) ₂ ²⁻
	51.207	HSO ₄ ⁻
	9.376	AlSO ₄ ⁺
	8.589	Al(SO ₄) ₂ ⁻
	1.27	FeSO ₄ (aq)
	8.361	FeSO ₄ ⁺
	1.88	Fe(SO ₄) ₂ ⁻
Competing coexisting sorbate species		
Fe ³⁺	5.356	Fe ⁺³
	0.2	FeOH ²⁺
	84.897	FeSO ₄ ⁺
	9.546	Fe(SO ₄) ₂ ⁻
Fe ²⁺	60.791	Fe ⁺²
	39.209	FeSO ₄ (aq)
Al ³⁺	10.008	Al ³⁺
	61.72	AlSO ₄ ⁺
	28.272	Al(SO ₄) ₂ ⁻

Table 3. Calculated adsorption energy using the Monte Carlo method.

Mineral	Clay type	Plane	Adsorption energy, kcal/mol	
			Single	Compete
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	(0 0 1)	-1014.05	-1147.97
Illite	K _{0.78} Ca _{0.02} Na _{0.02} Mg _{0.34} Al _{2.34} Fe _{0.02} Si _{3.35} O ₁₀ (OH) ₂ H ₂ O _n	(1 1 -1)	-1058.98	-1113.78
Palygorskite 121	Al Mg Si ₄ O _{10.4}	(1 2 -1)	-1017.73	-1091.46
Palygorskite 220	Al Mg Si ₄ O _{10.4}	(2 2 0)	-1045.42	-1182.72
Biotite	K ₂ (Fe _{2.786} Mg _{2.321} Ti _{0.550}) (Al _{2.413} Si _{5.587} O ₂₀) (OH) ₄	(1 3 5)	-983.73	-1085.68
Vermiculite	Si _{5.54} Al _{2.36} Fe _{0.12} Mg _{4.38} Al _{0.96} Fe _{0.28} Ti _{0.08} F _{0.30} (OH) _{3.70} O ₂₀ Ca _{0.9} (H ₂ O) _{6.32}	(0 0 1)	-1034.20	-1134.96
Montmorillonite	Ca _{0.5} Al ₂ Si ₄ O ₁₂	(0 0 1)	-977.36	-1090.47
Nontronite	Fe Si ₂ O ₆ H	(0 0 1)	-1049.57	-1143.34
Zincite	ZnO	(1 0 1)	-952.20	-1083.09
Franklinite	ZnFe ₂ O ₄	(1 1 1)	-928.26	-1057.81

It is known that bentonite is complex clay mineral of silicate group consisted from montmorillonite, illite, kaolinite and etc. Montmorillonite is main component of bentonite, it has a layered structure suitable for water sorption and swelling. It provides bentonite unique properties, such as gel formation and high adsorption capacity. The sorption of U(VI) by kaolinite and illite can be influenced by a number of environmental factors, including

coexisting cations and anions, as well as natural organic substances, etc. [1]. In contrast, mineral waste materials like ZnO and ZnFe₂O₄ can be accumulated from various industrial production of zinc-containing ores and dust of steel-making industry. Appropriate disposal of mineral waste materials are crucial to reduce their environmental impact and ensure the safety of human health [7-10].

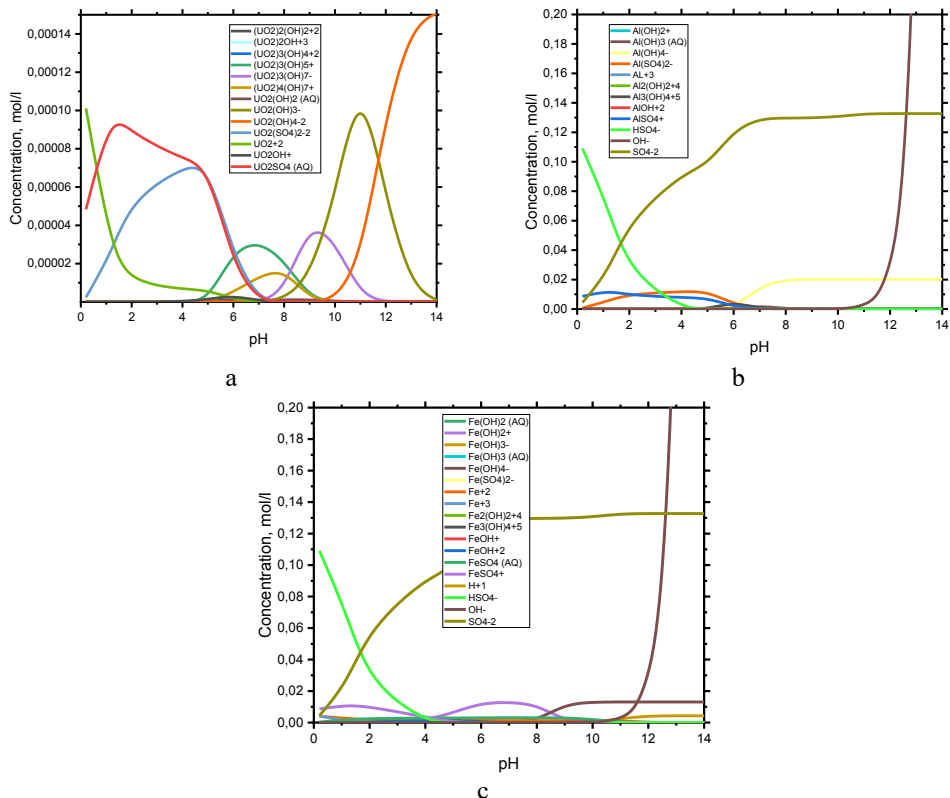


Fig. 2. Species diagram of U(VI) in solutions.

Typically, more negative adsorption energies (E_{ads}) indicate higher adsorption between the sorbate particles and the sorbent's surface. High negative values of $E_{ads} \sim -1000$ kcal/mol mean high stability of the adsorption system and high possibility of achieving spontaneous adsorption in the system. It was found that all studied clay sorption materials have a high absolute value of E_{ads} , and, therefore, demonstrate high sorption efficiency of model uranium solutions for single (UO_2^{2+} , UO_2SO_4 , $UO_2(SO_4)_2^{2-}$, H_2SO_4 , HSO_4^- , SO_4^{2-}) and compete (UO_2^{2+} , UO_2SO_4 , $UO_2(SO_4)_2^{2-}$, $AlSO_4^+$, $Al(SO_4)_2^-$, $FeSO_4^-$, H_2SO_4 , HSO_4^- , SO_4^{2-}) sorbates in sulfuric acid solutions at pH=1,2.

3.2 Analysis of differential heat of adsorption for single and competing sorption in H₂SO₄ solutions

The values of the differential heats of adsorption are given in Table 4. According MC simulation results, different U(VI) species in the single uranium sorbate are adsorbed on different mineral crystalline planes with different energies. Cationic particles UO_2^{2+} have the maximum adsorption energy for illite ($E_{ads} = -532$ kcal/mol) and the lowest for palygorskite ($E_{ads} = -452$ kcal/mol), and anionic particles $UO_2(SO_4)_2^{2-}$ are better sorbed on vermiculite

($E_{\text{ads}} = -333$ kcal/mol) and nontronite ($E_{\text{ads}} = -350$ kcal/mol) and worse on montmorillonite ($E_{\text{ads}} = -289$ kcal/mol) and kaolinite ($E_{\text{ads}} = -287$ kcal/mol), respectively. For neutral particles UO_2SO_4 the adsorption energy values slightly deviated within the range $E_{\text{ads}} = -29$ -4 kcal/mol, while montmorillonite is characterized by the lowest adsorption value on the surface in a sulfate solution containing U(VI) (Table 4).

Table 4 summarized data of the differential heat of adsorption (dE_{ads}/dN_i) for single (UO_2^{2+} , UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, H_2SO_4 , HSO_4^- , SO_4^{2-}) and compete (UO_2^{2+} , UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, AlSO_4^+ , $\text{Al}(\text{SO}_4)_2^-$, FeSO_4 , H_2SO_4 , HSO_4^- , SO_4^{2-}) sorption in sulfuric acid solutions at pH=1,2. It should be noted that dE_{ads}/dN_i are ranged as Al(III) (AlSO_4^+ ($E_{\text{ads}} = -120$ -63 kcal/mol), $\text{Al}(\text{SO}_4)_2^-$ ($E_{\text{ads}} = -133$ -51 kcal/mol)) and Fe(II/III) (FeSO_4^+ ($E_{\text{ads}} = -183$ -81 kcal/mol)). In generally, competing of coexisting ions should decrease sorption of uranium species on the clay and waste materials, however, vermiculite showed better affinities to any uranium species in presence of the Fe/Al species. In contrast, the UO_2^{2+} species showed better sorption on many clay surfaces (montmorillonite, vermiculite, nontronite, palygorskite 220) in presence of coexisting ions. Surprisingly, the UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ species have increased adsorption energies to illite surface but UO_2SO_4 also showed best affinity to nontronite in presence of Fe/Al ions.

Table 4. Calculated differential heats of adsorption (dE_{ads}/dN_i) for individual sorbate particles.

Mineral	UO_2^{2+}		UO_2SO_4		$\text{UO}_2(\text{SO}_4)_2^{2-}$	
	Single	Compete	Single	Compete	Single	Compete
Illit	-532.78	-430.79	-8.42	-19.77	-322.23	-378.43
Kaolinite	-503.49	-473.29	-10.28	-16.79	-287.53	-275.96
Palygorskit 121	-501.10	-428.17	-22.71	-7.89	-294.06	-238.67
Montmorillonite	-490.26	-521.98	-3.90	-5.22	-289.96	-254.22
Biotite	-478.52	-421.57	-28.80	-8.04	-305.41	-265.81
Vermiculite	-472.01	-516.01	-10.25	-12.23	-333.85	-363.80
Nontronite	-472.45	-499.70	-7.77	-34.74	-350.50	-274.13
Palygorskit 220	-451.91	-522.86	-27.35	-7.55	-314.30	-263.36
Zincite	-533.61	-454.96	-3.56	-4.12	-309.77	-281.28
Franklinite	-476.41	-368.29	-13.95	-18.61	-289.48	-336.90

These results can be used for explanation of experimental data and prediction of higher values of the exchange capacity of different clays during *in-situ* leaching of uranium.

4 Conclusions

The Monte Carlo molecular modelling revealed different sorption energy values of the U(VI), Al(III), Fe(II/III) species (UO_2^{2+} , UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, AlSO_4^+ , $\text{Al}(\text{SO}_4)_2^-$, FeSO_4) in acidic sulfate solutions (H_2SO_4 , HSO_4^- , SO_4^{2-}) on the surface of the clay (kaolinite, illite, palygorskite, biotite, vermiculite, montmorillonite, nontronite) and waste (zincite, franklinite) materials. The sorption energy has following order: UO_2^{2+} ($E_{\text{ads}} = -532$ -421 kcal/mol) > $\text{UO}_2(\text{SO}_4)_2^{2-}$ ($E_{\text{ads}} = -350$ -275 kcal/mol) > FeSO_4^+ ($E_{\text{ads}} = -183$ -81 kcal/mol) > $\text{Al}(\text{SO}_4)_2^-$ ($E_{\text{ads}} = -133$ -51 kcal/mol) > AlSO_4^+ ($E_{\text{ads}} = -120$ -63 kcal/mol) > UO_2SO_4 ($E_{\text{ads}} = -35$ -4 kcal/mol). The coexisting Fe/Al species can increase sorption of uranium species on vermiculite in the sulfate acid solutions. The UO_2^{2+} species showed better sorption on many materials surfaces (montmorillonite, vermiculite, nontronite, palygorskite) in presence of

competing ions. The Fe/Al species enhanced adsorption energies to illite and franklinite surfaces.

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