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U.S. Nuclear Regulatory Commission
ATTN: Mrs. Deborah A. DeMarco
2 White Flint North
11545 Rockville Pike
Mail Stop T8A23
Washington, DC 20555

Subject: Programmatic Review of Abstract

Dear Mrs. DeMarco:

The enclosed abstract is being submitted for programmatic review. This abstract will be submitted for presentation at the 24th International Symposium on the Scientific Basis for Nuclear Waste Management, to be held in Sydney, Australia, August 27–31, 2000, The title of the abstract is:

"Molecular Simulation of Uranium(6+) Adsorption on Quartz Surfaces"
by Jeffery Greathouse and Roberto T. Pabalan

This abstract is a product of CNWRA and NRC staff members, and it does not necessarily reflect the view(s) or regulatory position of the NRC.

Please advise me of the results of your programmatic review. Your cooperation in this matter is appreciated.

Sincerely,

Budhi Sagar
Technical Director

/ar
Enclosure

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MRS 2000 24th International Symposium on the Scientific Basis for Nuclear Waste Management

MOLECULAR SIMULATION OF URANIUM(6+) ADSORPTION ON QUARTZ SURFACES. Jeffery Greathouse, Department of Chemistry, St. Lawrence University, Canton, New York,USA; Roberto T. Pabalan, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, USA.

An important mechanism for attenuating radionuclide migration from nuclear waste repositories to the biosphere is the sorption of radionuclides on minerals encountered along groundwater flow paths. However, the effectiveness of this retardation mechanism depends on the physicochemical characteristics of mineral sorbents and the chemistry of radionuclide-bearing groundwater. In this study, the adsorption of uranyl species onto quartz surfaces was investigated using molecular simulation techniques. The influence of aqueous chemistry (e.g., pH, pCO_2) on uranyl sorption was indirectly studied by simulating the adsorption of different uranyl species (e.g., aquo-, hydroxo- and carbonato-complexes) whose stabilities are strongly dependent on solution composition. The energetics and structure of these species in vacuo and in an aqueous environment were evaluated using molecular dynamics (MD) simulation, with force field parameters derived from the literature. The results are in good agreement with experimental data. The interaction of the aqueous uranyl species with quartz surfaces, which have adsorption sites that are either predominantly protonated or predominantly deprotonated, was studied using energy minimization and MD. The adsorption simulation results are generally consistent with published sorption data.

This abstract is an independent product of the Center for Nuclear Waste Regulatory Analyses and does not necessarily reflect the views or regulatory position of the U.S. Nuclear Regulatory Commission.

SUMMARY[1]

An important mechanism for attenuating radionuclide migration from nuclear waste repositories to the biosphere is the sorption of radionuclides on minerals encountered along groundwater flow paths. However, the effectiveness of this retardation mechanism depends on geochemical factors such as the physicochemical characteristics of mineral sorbents and the chemistry of radionuclide-bearing groundwater. The effects of these factors on sorption processes are typically determined through sorption experiments, and spectroscopic techniques, such as extended X-ray absorption fine structure (EXAFS) spectroscopy, have been used to directly probe the structure of sorbed species.

Molecular modeling techniques serve as a useful complement to sorption experiments and spectroscopic methods. In this study, molecular simulation techniques were used to study the adsorption of uranyl (U^{6+}) species on quartz surfaces. The influence of aqueous chemistry (e.g., pH, pCO_2) on uranyl sorption was indirectly studied by simulating the adsorption behavior of different uranyl species whose stabilities are strongly dependent on solution composition. The potential effect on sorption of the mineral surface charge was investigated by modeling quartz surfaces with either predominantly protonated or predominantly deprotonated sorption sites. The energetics and structure of the uranyl complexes and the local solution environment in the bulk and adsorbed states were determined from energy minimization and molecular dynamics (MD) simulations. Structural information derived from the simulations were compared with those derived from x-ray diffraction and spectroscopy, and relative energies of sorption interactions were compared with observations from sorption measurements.

The models were constructed and simulations were performed on a Silicon Graphics workstation using the software package Cerius-2 Version 3.9 developed by Molecular Simulations, Inc. (San Diego, California). This suite of software has the capability of performing energy minimization and MD calculations based on several types of generic intermolecular force fields. Each of the commonly used force fields represents molecules as collections of interaction sites or atoms. Force fields are considered semi-empirical because they employ expressions that are approximate representations of interatomic interactions. However, the expressions enable rapid evaluation of the forces.

The models considered in this study include water, the uranyl (UO_2^{2+}) cation, and the carbonate (CO_3^{2-}), nitrate (NO^-), and hydroxide (OH^-) anions. A {010} α-quartz surface, approximately 10 Å thick and with lateral dimensions of 30 Å × 30 Å, was constructed for the adsorption studies with the crystal building tools of Cerius-2. Singly protonated sites were constructed by attaching a proton to each dangling oxygen at the surface. The surface atoms, with the exception of the protons, were held fixed in the MD simulations. Simulations in bulk solvent were performed using three-dimensional periodic boundary conditions, with long-range forces calculated using an Ewald sum technique.

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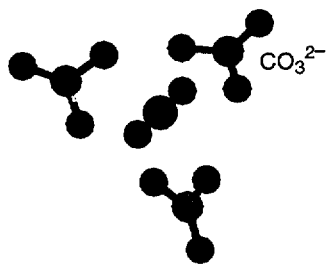
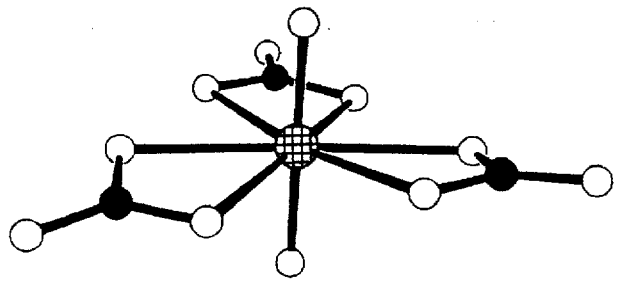
[1]This work was funded by the U.S. Nuclear Regulatory Commission (NRC). This summary is an independent product of the Center for Nuclear Waste Regulatory Analyses (CNWRA) and does not necessarily reflect the views or regulatory position of the NRC. The software Cerius-2 Version 3.9 is being placed into CNWRA configuration control.

Examples of the simulation results are shown below:

1. Structure of aqueous uranyl carbonato-complex — comparison of simulation result and XRD data

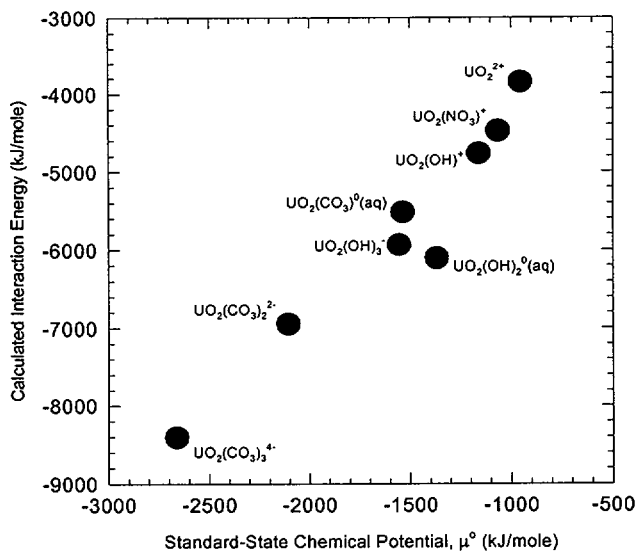


Ball-and-stick representation of the $UO_2(CO_3)_3^{4-}$ complex extracted from simulation in an aqueous environment. The uranyl ion is coordinated in the equatorial plane to six oxygens from three CO_3^{2-} ligands.

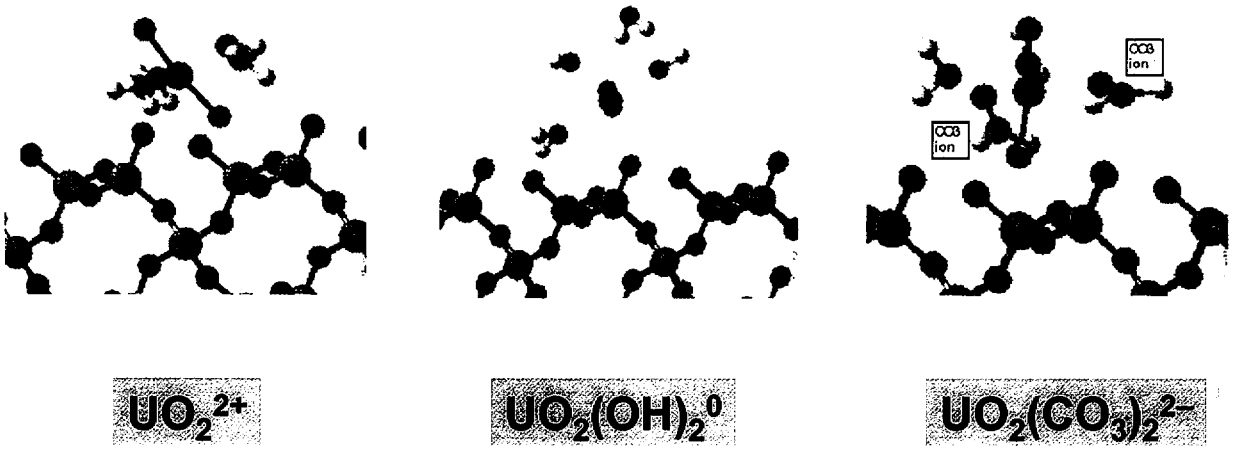


Ball-and-stick drawing illustrating the hexagonal bipyramidal coordination geometry in the solid structure of $UO_2(CO_3)_3^{4-}$ complexes (from Clark et al., 1995, Chem. Rev. **95**, 25)

2. Comparison of interaction energies derived from the simulations and published standard chemical potential for aqueous uranyl species



3. Structure of UO_2^{2+}, $UO_2(OH)_2^{o}$, and $UO_2(CO_3)_2^{2-}$ adsorbed on deprotonated quartz sites (in vacuo)



4. Table illustrating the structure and energetics of uranyl complexes sorbed on deprotonated quartz derived from MD simulations. Negative interaction energies indicate the sorption reaction is favorable. The negative energies of interaction between the uranyl hydroxy species and the quartz surface are consistent with experimental data that show uranyl sorption occurs in the pH range where hydroxy complexes are predominant. The positive interaction energy between the uranyl carbonate complex and quartz is also consistent with sorption data that show uranium does not sorb well from solutions where carbonate ligands are present.

Complexing Ligand(s)	x (No. of H_2O)	Coordination Number				Energy
		O_w	O_{ion}	O_{qtz}	Total	(kJ/mol)
None	5	4	-	1	5	-1600
NO_3	3	2	2	1	5	-1225
OH	4	2	1	1	4	-1464
$(OH)_2$	3	1	2	1	5	-1116
$(OH)_3$	2	1	3	1	5	-2029
CO_3	4	3	2	0	6	1027