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Author

Rao, Linfeng

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The effect of temperature on the speciation of U(VI) in sulfate solutions

Linfeng Rao, Guoxin Tian

Lawrence Berkeley National Laboratory, Berkeley, California 94720, U.S.A.

Abstract. Sulfate, one of the inorganic constituents that could be present in the nuclear waste repository, forms complexes with U(VI) and affects its migration in the environment. Results show that the complexation of U(VI) with sulfate is enhanced by the increase in temperature. The effect of temperature on the complexation and speciation of U(VI) in sulfate solutions is discussed.

Introduction

Uranium is the most abundant radioactive element in the nuclear wastes generated by the nuclear industry including uranium mining and spent nuclear fuel reprocessing. Safe management of the nuclear wastes, the high-level nuclear wastes (HLW) in particular, calls for proper treatment and long-term disposal in geological repositories. Engineered barrier systems (e.g., waste packaging and drip shields) are implemented to prevent the waste forms from being eroded and/or breached. Though the engineered barrier systems are expected to last a very long time after the repository is closed, they may gradually deteriorate and eventually lose integrity. If this disastrous scenario occurs, water could contact the waste form, dissolve it, and carry radionuclides out of the repository. The migration of radionuclides, including uranium, in the post-closure environment of the repository is a great concern to the long-term performance assessment of the nuclear waste repository.

Complexation of U(VI) with inorganic ligands that exist in the groundwater of the repository (e.g., OH^- , F^- , SO_4^{2-} , PO_4^{3-} and CO_3^{2-}) could affect the speciation of U(VI) and its migration in the environment. Moreover, the temperature of the HLW repository could remain significantly higher than the ambient even thousands of years after the closure of the repository. As Fig. 1 shows, the projected temperature in the vicinity of the waste form in the Yucca Mountain Repository of the United States is around 80-100°C, even a thousand years after the closure of the repository (OCRWM 2002). As a result, predictions of the migration behavior of U(VI) in the repository cannot be made without taking into consideration the

effect of temperature on the complexation of U(VI) with the ligands that may exist in the groundwater of the repository. Unfortunately, data on the complexation of U(VI) with many inorganic as well as organic ligands at elevated temperatures are not available at present (Grenthe et al. 1992, Guillaumont et al. 2003). To help with the performance assessment of the HLW repository and fill the gap in thermodynamic data on actinide complexation at elevated temperatures, we have studied the complexation of actinides with selected organic and inorganic ligands at elevated temperatures. This paper briefly summarizes the results on the complexation of U(VI) with sulfate at elevated temperatures and discusses the effect of temperature on the speciation of U(VI) in sulfate solutions.

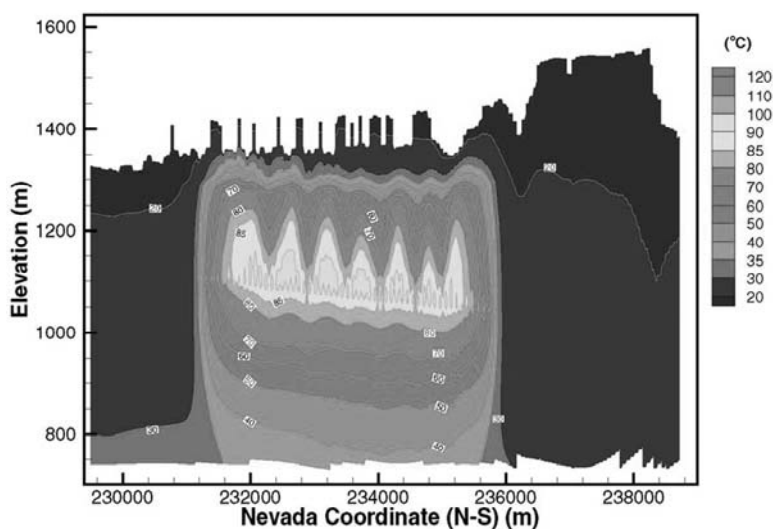


Fig. 1. Temperature distribution at 1,000 years along NS#2 cross section of Yucca Mountain Repository (with ventilation) from the Mountain-Scale Thermal-Hydrologic Model (OCRWM 2002). The color band indicates that the temperature of the waste forms (200 - 300 meters below the ground surface) is around 80 – 100°C.

Experimental

Chemicals

All chemicals were reagent grade or higher. Milli-Q water was used in preparations of all solutions. Preparation and standardization of the stock solution of uranyl perchlorate have been described elsewhere (Zanonato et al. 2004). A stock

solution of sodium sulfate was prepared by dissolving appropriate amounts of sodium sulfate solid in water. The ionic strength of all solutions used in spectrophotometric titrations was adjusted to 1.0 M Na(ClO₄/SO₄) at 25°C. All the molar concentrations in this paper are referred to 25°C.

Variable-temperature spectrophotometry

UV/Vis absorption spectra of U(VI) (380 - 480 nm, 0.2 nm interval) were collected on a Varian Cary-5G spectrophotometer equipped with sample holders that were maintained at constant temperatures by a 1×1 Peltier controller. 10 mm quartz cells were used. Before being inserted into the sample holders, the sealed cells were immersed in an external constant-temperature water bath to be pre-equilibrated at the required temperature. This procedure successfully prevented condensation of water on the top of the cells during the titrations at high temperatures. Multiple titrations with different concentrations of U(VI) were performed. In each titration, appropriate aliquots of the Na₂SO₄ solution were added into the cell and mixed thoroughly before the absorption spectrum was collected. Usually 10 - 15 spectra were collected in each titration. Stability constants of the U(VI)/sulfate complexes (on the molarity scale) were calculated by non-linear least-square regression using the Hyperquad program (Gans et al. 1996).

Results and discussion

Stability constants of U(VI)/sulfate complexes at variable temperatures (25 – 70°C)

Spectrophotometric titrations were conducted at 25, 40, 55 and 70°C. The absorption spectra of a representative titration at 55°C are shown in Fig. 2. The first spectrum (the bottom one) shows the characteristic vibronic bands of free UO₂²⁺ in the UV/Visible region ($\lambda_{\text{max}} \approx 414$ nm). Two distinct changes were observed as the concentration of sulfate was increased: (1) the positions of the absorption bands of U(VI) were shifted to longer wavelengths; (2) the absorbance of U(VI) solutions increased significantly. Both changes suggest that U(VI)/sulfate complex(es) formed. Factor analysis of the absorption spectra by the Hyperquad program indicate that there are three absorbing species of U(VI), i.e., free UO₂²⁺ and two U(VI)/sulfate complexes. Therefore, the spectra were best-fit with the formation of successive 1:1 and 1:2 complexes, UO₂SO₄(aq) and UO₂(SO₄)₂²⁻, represented by equations 1 and 2.



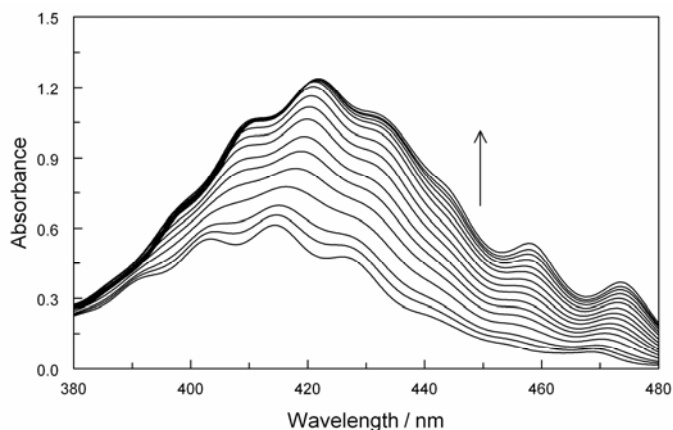


Fig. 2. A representative spectrophotometric titration of U(VI)/sulfate complexation at 55°C. $I = 1.0$ M Na(ClO₄/SO₄). Initial solution: 2.50 mL, 0.071 M UO₂(ClO₄)₂/0.085 M HClO₄; titrant: 0.5 M Na₂SO₄. Final solution: 6.08 mL. The arrow indicates the increase of the sulfate concentration. The spectra are normalized for the concentration of U(VI).

The stability constants of UO₂SO₄(aq) and UO₂(SO₄)₂²⁻ at 25, 40, 55 and 70°C were calculated and summarized in Table 1. In the calculation, the protonation constants of sulfate at different temperatures from the literature were used (Rao et al. 2006). Data in Table 1 indicate that U(VI) forms moderate complexes with sulfate and the complexes become stronger at higher temperatures – 2-fold and 10-fold increases in the values of β for UO₂SO₄(aq) and UO₂(SO₄)₂²⁻, respectively, as the temperature is increased from 25 to 70°C.

Table 1. Equilibrium constants of the protonation and complexation of sulfate with U(VI).

Reaction	$T/^\circ\text{C}$	Method ^a	$\log \beta$ ($I = 1.0$ M)	Ref. ^b
$\text{H}^+ + \text{SO}_4^{2-} = \text{HSO}_4^-$	25	cal	1.07 ± 0.09	(Rao et al. 2006)
	40	cal	1.14 ± 0.12	
	55	cal	1.28 ± 0.09	
	70	cal	1.38 ± 0.09	
$\text{UO}_2^{2+} + \text{SO}_4^{2-} = \text{UO}_2\text{SO}_4(\text{aq})$	25	sp	1.96 ± 0.06	p.w.
	40	sp	2.04 ± 0.06	
	55	sp	2.20 ± 0.06	
	70	sp	2.32 ± 0.03	
$\text{UO}_2^{2+} + 2\text{SO}_4^{2-} = \text{UO}_2(\text{SO}_4)_2^{2-}$	25	sp	2.97 ± 0.03	p.w.
	40	sp	3.34 ± 0.03	
	55	sp	3.71 ± 0.06	
	70	sp	3.94 ± 0.15	

^a Method: cal – calorimetry; sp - spectrophotometry.

^b p.w. – present work.

Speciation of U(VI) in sulfate solutions at variable temperatures

The stability constants of U(VI)/sulfate complexes in Table 1, in conjunction with the equilibrium constants of U(VI) hydrolysis at elevated temperatures in the literature (Zanonato et al. 2004), allow us to calculate the speciation of U(VI) in sulfate solutions at variable temperatures as a function of acidity. The calculated speciation diagrams at 25 and 70°C are shown in Fig. 3.

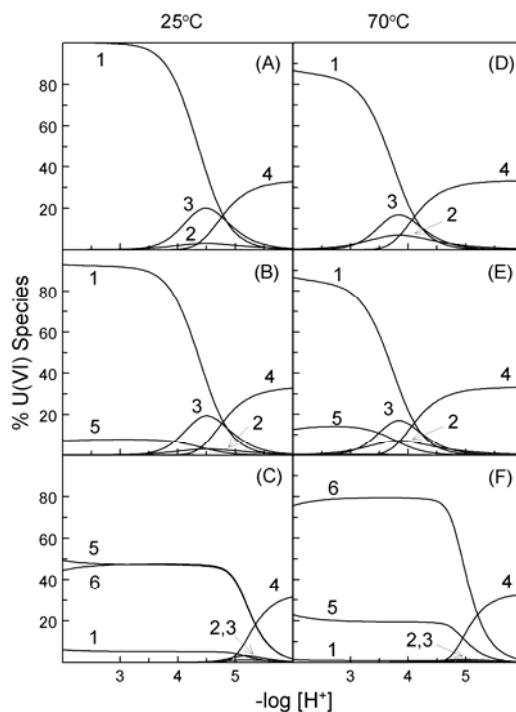


Fig. 3. Speciation of U(VI) as a function of acidity in sulfate solutions at 25 and 70°C ($I = 1.0$ M). $C_{\text{U(VI)}} = 1.00$ mM. $C_{\text{sulfate}} = 0$ mM (A, D), 1.00 mM (B, E), 100 mM (C, F). Temperature: 25°C (A, B, C), 70°C (D, E, F). Species: 1 - free UO_2^{2+} , 2 - UO_2OH^+ , 3 - $(\text{UO}_2)_2(\text{OH})_2^{2+}$, 4 - $(\text{UO}_2)_3(\text{OH})_5^+$, 5 - $\text{UO}_2\text{SO}_4(\text{aq})$, 6 - $\text{UO}_2(\text{SO}_4)_2^{2-}$.

At 25°C, in the absence of sulfate (Diagram A), the hydrolysis of U(VI) starts at about pC_H (i.e., $-\log[\text{H}^+]$) 3.5 and the trimeric $(\text{UO}_2)_3(\text{OH})_5^+$ species becomes dominant when $\text{pC}_\text{H} > 5$. The presence of 1 mM sulfate (Diagram B) only slightly changes the speciation. However, the presence of 100 mM sulfate (Diagram C) effectively suppresses the formation of the monomeric and dimeric hydrolysis species (UO_2OH^+ and $(\text{UO}_2)_2(\text{OH})_2^{2+}$), significantly altering the speciation of U(VI) in the low pC_H region (from 3.5 to 5). When the pC_H is above 5, formation of the

trimeric $(\text{UO}_2)_3(\text{OH})_5^+$ species starts and becomes dominant at higher pC_H , where the strength of U(VI)/sulfate complexes is not sufficiently high to compete with hydrolysis.

At 70°C, the trends in speciation as the sulfate concentration is increased from 0 (Diagram D), 1.00 mM (Diagram E) to 100 mM (Diagram F) are similar to those observed at 25°C. However, because both the hydrolysis of U(VI) and the complexation of U(VI) with sulfate are enhanced at higher temperatures, the speciation at 70°C differs from that at 25°C. In particular, the U(VI) sulfate complexes, $\text{UO}_2\text{SO}_4(\text{aq})$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$, dominate in the low pC_H region when the sulfate concentration is 100 mM, with $\text{UO}_2(\text{SO}_4)_2^{2-}$ accounting for 80% up to pC_H 5.

In summary, the presence of sulfate in high concentrations significantly affects the speciation of U(VI) in the low pC_H region (< 5), but has a negligible effect when $\text{pC}_\text{H} > 5$ where the higher hydrolysis species (e.g., $(\text{UO}_2)_3(\text{OH})_5^+$) forms. The importance of U(VI)/sulfate complexation and its effect on U(VI) speciation in the low pC_H region is more significant as the temperature increases.

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