

Stability of U(IV) sulfate complexes at elevated temperatures

VAN HARTESVELDT, N.^{1,2*}, MIGDISOV, A.¹, XU, H.¹,
ROBACK, R.¹, GABITOV, R.²

¹Los Alamos National Laboratory, Earth & Environmental
Division, Los Alamos, NM, USA (nvanhart@lanl.gov)

²Mississippi State University, Mississippi State, MS, USA

Limiting mobilization of uranium species in aqueous, saline solutions is of premier importance for managing radioactive waste, predicting effects of nuclear accidents, and understanding formation of ore deposits. U(VI) and U(IV) are the two most abundant uranium valence states; however, traditional paradigm assumes only the U(VI) state is mobile in hydrothermal solutions, while reducing conditions lead to the formation of reduced U(IV) oxides, which are highly insoluble¹.

Recent findings have challenged this paradigm. At elevated temperatures, U(IV) chloride species have been shown to be extremely stable, and can successfully compete in aqueous solutions with oxidized uranium species². Like chloride, sulfate is one of the most abundant ligands in natural systems³. Low temperature data suggests that uranium has a much higher affinity to sulfate than chloride⁴ – therefore it is logical to theorize that this affinity can be observed at elevated temperatures as well for U(IV). Problematically, data on the stability of U(IV) sulfate complexes at elevated temperatures are completely absent.

Therefore, this study reports experimentally determined stability of U(IV)/SO₄²⁻ complexes at saturated water pressure and temperatures up to 350°C. We base our technique on determination of the solubility of UO₂ in SO₄²⁻ bearing acidic solutions, using Ni/NiO and Co/CoO buffers to control redox conditions. This experimental design ensures predominance of U(IV) species in aqueous solutions and stability of UO₂.

This talk will present the first results obtained in this study, showing the contribution of sulfate complexes to the mass balance of U-bearing aqueous species can be significant at elevated temperatures. Preliminary calculations illustrating uranium speciation in natural hydrothermal solutions will also be presented.

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[3] Millero et al. (2008). The composition of standard seawater and the definition of the reference-composition salinity scale. *Deep Sea Research Part I: Oceanographic Research Papers*, 55(1), 50-72.

[4] Hennig et al. (2005). Comparative EXAFS investigation of uranium (VI) and-(IV) aquo-chloro complexes in solution using a newly developed spectro-electrochemical cell. *Inorganic chemistry*, 44(19), 6655-6661.