

Effect of Competing Complexing Cations and Humic Substances on Ligand-induced Mobilization of Non-crystalline U(IV) under Anoxic Conditions

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The ability of organic ligands to mobilize various reduced uranium (U) phases even under anoxic conditions poses a concern to the long-term stability of U immobilized in the subsurface. This concern is most pressing in the case of more labile tetravalent uranium (U(IV)) phases such as non-crystalline U(IV). In complex field environments the extent and rate of ligand-induced U mobilization can be impacted by numerous factors. Two such factors are the presence of other cations competing for complexation, and of humic substances (HS) competing for U binding.

To elucidate the impact of competing cations on ligand-induced U mobilization, experiments were carried out with non-crystalline U(IV) and a variety of structurally diverse organic ligands (low-molecular-weight organic acids, synthetic chelators, microbial siderophores) which were pre-complexed to cations. Competing cations included Ca^{2+} , Fe^{3+} , and Zn^{2+} . Also, the effects of HS were assessed in regards to U mobilization from non-crystalline U(IV) using Suwannee River humic and fulvic acids. Experiments were carried out to directly compare effects of humic and fulvic acids with those of other organic ligands on U mobilization, and to identify potential synergistic effects on U mobilization by HS and these organic ligands.

The presence of competing cations and humic substances were both shown to have substantial and differing effects on U mobility under anoxic conditions. Competing cation effects varied as a function of the affinity of each respective ligand for U and the competing cation while the effects of HS on U mobility depended on the HS type and which organic ligand the HS was paired with. These results highlight that depending on the cation or HS type, pre-complexation of competing cations or HS can strongly reduce the rate and extent of ligand-induced U mobilization. The findings of this work have implications regarding the stability of U(IV) phases in the subsurface, and thus, can be an aid in quantifying risks posed by organic ligands towards ligand-induced mobilization of U(IV) based on site specific conditions.