The Stability and Dissolution of Two Uranyl Peroxide Nanoclusters in Aqueous Solutions: U60 and U24P

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Uranyl peroxide nanoclusters represent a newly-discovered class of uranium compounds whose presence in aqueous solution could control the mobility and partitioning of uranium in the environment, however the stabilities and dissolution behaviors of these nanoclusters in aqueous solutions have not been determined. In this study, we measure the dissolution and stability of two uranyl peroxide nanoclusters: U60 ($K_{16}Li_{44}[UO_2(O_2)OH]_{60}$), a uranyl peroxide nanocluster with a diameter of 2.4 nm and a mass of 19,640 Da, and U24P ($Na_{30}[(UO_2)_{24}(O_2)_{24}(H_2P_2O_7)_6(H_2P_2O_7)_6]$), a uranyl peroxide pyrophosphate nanocluster with a diameter of 2.0 nm and a size of 10,566 Da. In each system, batch dissolution experiments were conducted as a function of equilibration time, nanocluster concentration and pH. Separation of the nanoclusters in each experiment from other aqueous species was accomplished using molecular weight filtration. Aqueous U, P, K, Li, and/or Na concentrations were measured by ICP-OES.

In the U60 dissolution experiments a steady-state was reached within 24 hrs. Electrospray ionization mass spectrometry has been used to show that U60 nanoclusters remain intact in solution for at least a year. The steady-state concentrations of aqueous U, K, and Li in the U60 experiments increased with increasing nanocluster concentration, and do not change significantly as a function of pH over the pH range 7.5 to 8.5. The solubility of bulk solid phases does not depend on the concentration of that phase in suspension; hence, the observed U60 dissolution behavior suggests that U60 behaves like an aqueous complex rather than a bulk solid phase, and the aqueous species concentrations are not buffered by the presence of the nanoclusters in solution.

In the U24P experiments in contrast to the U60 experiments, aqueous U and P concentrations increased continuously over the duration of the experiment, and never achieved steady state values. The U24P was found to remain intact in solution for 23 days, but significant degradation occurred after this time, and the electrospray ionization mass spectrometry signature of U24P was no longer observed after 44 days. U24P dissolution led to aqueous U and P concentrations that increased over 44 days of sampling, with the aqueous U amounting to the dissolution of approximately 8% of the initial nanocluster while for U60 aqueous U concentrations never exceed 3% of the initial nanocluster. Even though the U24P experiments never achieved steady state aqueous concentrations, at each sampling time the concentration of aqueous U was increased with increasing nanocluster concentration. This work documents significantly different behaviors of two nanocluster of the same class of uranium compounds and illustrates the dramatic differences in the potential fate of each type of nanocluster in the environment.