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Chemical equilibria in actinide carbonate systems

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By spectrophotometric and potentiometric methods it is shown that trimers are formed in media of high ionic strength (3 M $NaClO_4$) and total concentrations of hexavalent actinides higher than 10^{-3} M. The equilibrium constants for the reactions

$$3\ MO_2(CO_3)_3^{4-} \rightarrow (MO_2)_3(CO_3)_6^{6-} + 3\ CO_3^{2-}$$

are lg K(U) = −11.3 ± 0.1; lg K(Np) = −10.1 ± 0.1; lg K(Pu) = −7.4 ± 0.2. It is demonstrated that one of the cations of the trimer can be exchanged with another actinide cation: the equilibrium constants for the reactions

$$2\ UO_2(CO_3)_3^{4-} + MO_2(CO_3)_3^{4-} \rightarrow (UO_2)_2MO_2(CO_3)_6^{6-} + 3\ CO_3^{2-}$$

are lg K = −11.3 ± 0.1,−10.0 ± 0.2 and −8.8 respectively for M ≡ U, Np, Pu. Thus, polynuclear complexes can be efficient solution "carriers" for other hexavalent actinides in waste disposal. Some properties of the solid phases MO_2CO_3(s) are discussed.

Experimental studies of chemical equilibria of americium (III, IV) are reviewed: in carbonate media americium(III) species are $AmCO_3^+$, $Am(CO_3)_2^-$, $Am(CO_3)_3^{3-}$, $(Am_2(CO_3)_3)_s$ and $(NaAm(CO_3)_2)_s$; for americium-(IV) lg $\beta_5 \approx 40$.

In 3 M $NaClO_4$ solubility measurements of neptunium(V) show that lg β_1 = 5.09, lg β_2 = 8.15, lg β_3 = 10.46, lg Ks($NaNpO_2CO_3$) = -10.56 and lg Ks($Na_3NpO_2(CO_3)_2$) = -12.44; ionic strength corrections are proposed on the basis of these results.