A Thermodynamic Model for the Solubility of PuO_2(am) in the Aqueous K^+-HCO_3^--CO_3^{2-} -OH^--H_2O System

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The solubility of PuO_2(am) was determined in the aqueous K^+-HCO_3^--CO_3^{2-} -OH^--H_2O system extending to high concentrations of carbonate and bicarbonate. X-ray absorption spectroscopy (XAS) and solvent extraction were used to identify species and oxidation states in the aqueous phase. The dominant aqueous species in relatively concentrated CO_3^{2-} and HCO_3^- solutions were determined by XAS to be $Pu(CO_3)_5^{6-}$. The solubility of PuO_2(am) increased dramatically with increasing total carbonate concentrations, indicating that carbonate makes strong complexes with Pu(IV). The dominant Pu(IV)-carbonate species that reasonably described all of the experimental data were $Pu(CO_3)_5^{6-}$ in high concentrations of carbonate and bicarbonate and $Pu(OH)_2(CO_3)_2^{2-}$ in low concentrations of bicarbonate. Data suggest the possible presence of another species in the low carbonate and high pH region. However, because of uncertainty in Pu(IV) concentrations in this region, no attempt was made to fit the data in this region. The logarithm of the thermodynamic equilibrium constants for the PuO_2(am) dissolution reactions involving$Pu(CO_3)_5^{6-}$ and $Pu(OH)_2(CO_3)_2^{2-}$ [(PuO_2(am) + 5 CO_3^{2-} + 4 H^+ $\leftrightarrows$ $Pu(CO_3)_5^{6-}$ + 2 H_2O) and (PuO_2(am) + 2 HCO_3^- $\leftrightarrows$ $Pu(OH)_2(CO_3)_2^{2-}$)] were found to be 33.32 and -4.78, respectively. These values, when combined with the solubility product of PuO_2(am) (log K_{sp} = -56.85 [1]), provided logarithm of the equilibrium constants of 34.18 and 44.76, respectively, for (Pu^{4+} + 5 CO_3^{2-} $\leftrightarrows$ $Pu(CO_3)_5^{6-}$) and (Pu^{4+} + 2 CO_3^{2-} + 2 OH^- $\leftrightarrows$ $Pu(OH)_2(CO_3)_2^{2-}$.