



**Thermodynamic model for the solubility of PuO₂(am) in
the aqueous
Na⁺-H⁺-OH⁻-Cl⁻-H₂O-ethylenediaminetetraacetate
system**

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► **To cite this version:**

Dhanpat Rai, Heather Bolton, Da. Moore, Nancy Hess, G. Choppin, et al.. Thermodynamic model for the solubility of PuO₂(am) in the aqueous Na⁺-H⁺-OH⁻-Cl⁻-H₂O-ethylenediaminetetraacetate system. Radiochimica Acta, 1999, 86 (3-4), pp.89-99. 10.1524/ract.2001.89.2.067 . cea-02359297

HAL Id: cea-02359297

<https://cea.hal.science/cea-02359297>

Submitted on 2 Dec 2019

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A Thermodynamic Model for the Solubility of $\text{PuO}_2(\text{am})$ in the Aqueous $\text{K}^+ \text{-HCO}_3^- \text{-CO}_3^{2-} \text{-OH}^- \text{-H}_2\text{O}$ System

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The solubility of $\text{PuO}_2(\text{am})$ was determined in the aqueous $\text{K}^+ \text{-HCO}_3^- \text{-CO}_3^{2-} \text{-OH}^- \text{-H}_2\text{O}$ 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 $\text{Pu}(\text{CO}_3)_5^{6-}$. The solubility of $\text{PuO}_2(\text{am})$ 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 $\text{Pu}(\text{CO}_3)_5^{6-}$ in high concentrations of carbonate and bicarbonate and $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ 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 $\text{PuO}_2(\text{am})$ dissolution reactions involving $\text{Pu}(\text{CO}_3)_5^{6-}$ and $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ [$(\text{PuO}_2(\text{am}) + 5 \text{CO}_3^{2-} + 4 \text{H}^+ \rightleftharpoons \text{Pu}(\text{CO}_3)_5^{6-} + 2 \text{H}_2\text{O})$ and $(\text{PuO}_2(\text{am}) + 2 \text{HCO}_3^- \rightleftharpoons \text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-})$] were found to be 33.32 and -4.78, respectively. These values, when combined with the solubility product of $\text{PuO}_2(\text{am})$ ($\log K_{\text{sp}} = -56.85$ [1]), provided logarithm of the equilibrium constants of 34.18 and 44.76, respectively, for $(\text{Pu}^{4+} + 5 \text{CO}_3^{2-} \rightleftharpoons \text{Pu}(\text{CO}_3)_5^{6-})$ and $(\text{Pu}^{4+} + 2 \text{CO}_3^{2-} + 2 \text{OH}^- \rightleftharpoons \text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-})$.