**Solubility, speciation and solid phase formation of**

**Pu(VI) in alkaline CaCl2 and NaCl solutions**

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**INTRODUCTION**

Within the An(VI) series, the hydrolysis behavior of Pu(VI) in aqueous solution shows some unique features that are clearly different from that of U(VI) and Np(VI). While U(VI) and Np(VI) readily form sparingly soluble An(VI)-(hydr)oxide solid phases in neutral to alkaline solutions, *e.g.* AnO2(OH)2⋅*x*H2O(cr), Na2An2O7⋅*x*H2O(cr) with An = U [1] and Np [2], and CaU2O7∙3H2O(cr) [3, 4], the hydrolytic behavior of Pu(VI) is dominated by the formation of dissolved polymeric hydrolysis products (PuO2)y(OH)x2y−x(aq). The latter are metastable, even at relatively high [Pu(VI)]tot [5], which becomes evident in the sluggish formation of Pu(VI)-(hydr)oxides. This challenge can explain why little is reported about the solubility behavior of Pu(VI)-(hydr)oxides. In this contribution we report on the successful preparation, characterization and solubility analysis of some Pu(VI)-(hydr)oxide solid phases in alkaline NaCl and CaCl2 solutions.

**DESCRIPTION OF THE WORK**

All experiments were performed at room temperature under inert Ar atmosphere with 242Pu. A freshly electrolyzed oxidation state pure 242PuO22+ stock solution was alkalinized with NaOH and with aqueous Ca(OH)2 suspension, respectively. Mild tempering for several weeks resulted in the formation of blackish (Na) and yellow-brownish (Ca) crystalline precipitates. The latter were investigated by powder XRD, SEM-EDX, chemical analysis by combined LSC+OES, Raman, thermogravimetric analysis, and XAFS at the *Karlsruhe Research Accelerator* (KARA). The solubility behavior were studied in 0.5-5.0 M NaCl solutions with pHm = 9-14 (blackish solid) and 0.25-2.0 M CaCl2 solutions with pHm = 9-12 (yellow-brownish solid phase) from undersaturation using hypochlorite as oxidizing agent. Several samplings of pHm = −log [H+]m (glass combination electrode), [Pu]tot (LSC) and [Pu(VI)] (liquid extraction) were performed as a function of time. Additional spectroscopic (Vis/NIR, EXAFS) investigations of the aqueous Pu(VI) speciation were performed.

**RESULTS AND DISCUSSION**

The results of the solid phase characterization shows that the blackish material precipitated in NaOH solution is a plutonate(VI) compound and consists of hexagonal platelets (SEM). Chemical analysis by EDX and by LSC+OES revealed an equimolar content of Na and Pu in the solid (Na : Pu ≈1:1). The compound is isostructural to Na2An2O7⋅*x*H2O(cr) with An = U [1] and Np [2] as confirmed by powder XRD. The blackish solid phase can therefore be identified as Na2Pu2O7⋅*x*H2O(cr). The yellow-brownish Pu(VI) solid phase precipitated in Ca(OH)2 solution consists of small rods (SEM) with a Ca : Pu ratio of 0.5 : 1 (EDX). Based on the XRD pattern, the solid phase is not isostructural with the uranate(VI)-like CaU2O7∙3H2O(cr) (hexagonal platelets) reported in [3]. The results are in agreement with an empirical formula Ca0.5PuO2(OH)3⋅*x*H2O(cr) (plutonyl(VI)-like structure). Thermogravimetric analysis of both solid phases to determine the content of crystal water will be performed at the end of the solubility study. Based on the initial data, both solid phases show a systematic increase of the Pu(VI) solubility with slope ≈+1 for pHm ≥ 11.5 which can be explained by PuO2(OH)42− as predominant Pu(VI) aqueous species under these conditions:

0.5 Na2Pu2O7⋅*x*H2O(cr) + (2.5−0.5x) H2O(l) ⬄ Na+ + PuO2(OH)42− + H+

and

Ca0.5PuO2(OH)3⋅*x*H2O(cr) + (1−x) H2O(l) ⬄ 0.5 Ca2+ + PuO2(OH)42− + H+.

For U(VI) (and Np(VI) in NaCl solutions), an analogous behaviour was observed [1, 2]. Details of the solubility behaviour, especially the data obtained for the less alkaline region, and from the results of additional solution Vis/NIR investigations will be discussed in our contribution.

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