

Actinide(IV) in carbonate media

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To predict the geochemical behaviour of Neptunium and Plutonium, or to design sorption or migration experiments with these radioelements, one needs to know their speciation in reducing aqueous solutions at pH 6 to 11, containing some carbonate ions. Their solubility is very low (10^{-8} to less than 10^{-10} mol./l), and is quite difficult to measure. The solid seems to be an amorphous Actinide(IV) hydroxide, that slowly transforms to a more crystalline phase, probably the Actinide(IV) oxide. Aqueous speciation is strongly dependent on the redox conditions. Most of the interpretations of the published Np(IV) or Pu(IV) solubility measurements are then questionable. Rai and Ryan (1985) already discussed this, and showed, that $[\text{CO}_3^{2-}]$ must probably be more than 0.01 mol./l to complex Np(IV). The limiting carbonate complex of U(IV) is (Grenthe et al. 1992) $\text{U}(\text{CO}_3)_5^{6-}$ and it dissociates into $\text{U}(\text{CO}_3)_4^{4-}$. This highly charged anion has also been identified in Ce(IV), Th(IV), and probably Np(IV) and Pu(IV) solid phases; but there are not enough correct experimental measurements to determine the stoichiometry of the soluble carbonate complexes of these elements. As stated above, precise experiments are difficult. The aim of this work is then mainly to confirm, that all these f transition elements at the +4 oxidation state, have the same behaviour in concentrated carbonate media.

Assuming the formation of $\text{An}(\text{OH})_4$, $\text{An}(\text{CO}_3)_4^{4-}$ and $\text{An}(\text{CO}_3)_5^{6-}$ (An= Np, Pu or Am), the speciation is calculated and it is enough to explain most of the published work (solubility, spectrophotometric and electrochemical behaviour of these elements). Still a few published solubility data are higher than the calculated ones. This is probably an evidence for other soluble hydroxocarbonate complexes. As stated above, this increase of solubility might also often be attributed to experimental artefacts, any conclusion on the stoichiometry and stability of such complex would then be very poorly reliable.

Np(IV) and Pu(IV) are prepared by electrochemical reduction in concentrated Na_2CO_3 solutions. The titration into NaHCO_3 by bubbling CO_2 gas, is followed by spectrophotometry. As for U(IV), the spectral changes are consistent with the lost of one CO_3^{2-} anion, (and no OH^-) over several pH units. These experiments are performed mainly in bicarbonate solutions. In too alkaline carbonate solutions, solubility is too low to use this methodology. All this confirms the U-Np-Pu-Am(IV) analogy for the stability of their limiting complex. The equilibrium constants are extrapolated to standard conditions by using the SIT and are used to discuss the preparation conditions of Am(IV) in bicarbonate/carbonate media (1983 Bourges et al.), and other actinide(IV) published results. It is finally shown, that the measurement of the Np(V)/Np(IV) and Pu(VI)/Pu(IV) redox potential can be used to determine the stoichiometry of these actinide(IV) limiting complexes.

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