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ABSTRACT FORM

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TDB REVIEW OF Np(IV) IN AQUEOUS CARBONATE SOLUTIONS

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It has been shown (Rai and Ryan 1985), that most of the interpretations of the published Np(IV) or Pu(IV) solubility measurements are questionable. Even now, a critical bibliography on Np(IV) carbonate chemistry (part of a chapter (Vitorge 1995) for the Thermodynamic Data Base of the NEA-OECD) still clearly shows the lack of reliable data; but it suggests a possible interpretation of most published work assuming, that, as uranium (Grenthe et al. 1992), all the f transition elements at the +4 oxidation state, M, form $M(\text{CO}_3)_4^{4-}$ and $M(\text{CO}_3)_5^{6-}$ soluble complexes with similar stability. Only a few published solubility data are then higher than the calculated ones. This is probably an evidence for other soluble hydroxocarbonate complexes; but 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.

The above interpretation gives the optimum conditions to prepare the Np(IV), Pu(IV) or (Bourges 1983) Am(IV) limiting complex. The spectral changes of Np(IV) (Delmau 1995) and Pu(IV) (1992 and 1995 Capdevila) in concentrated Na^+ , $\text{CO}_3^{2-}/\text{HCO}_3^-$ solutions are consistent with the lost of one CO_3^{2-} anion, (and no OH^-) over several pH units. Only one very inaccurate measurement of the Np(V)/Np(IV) redox couple was published (Fedosseev et al. 1979) probably due to a poor control of key chemical conditions. Stable measurements have been recently obtained (Delmau 1995). They confirm this previous value. This and also the Pu(VI)/Pu(IV) redox potential could be used to determine the stoichiometry of these actinide(IV) limiting complexes; but they are too few correct published data. Np(III) and Pu(III) stability in carbonate media are shortly discussed. Activity coefficients are taken into account by using the SIT.

It is finally shown, that the set of Np(IV) equilibrium constants deduced from the above spectrophotometric and electrochemical data can explain most of the published data (except some of the solubility measurements, as stated above).

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