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The thermodynamics of Uranium(IV) oxide in aqueous solutions. Myths and realities

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The thermodynamics of uranium(IV) oxide has been largely investigated in the last decades. After the decay of uranium mineral exploration, the main driving force for these investigations has been the fact that UO_2(s) is the main component of the spent nuclear fuel matrix. Hence its stability and dissolution behaviour are utterly interesting for the safe disposal of the used fuel.

The predicted thermodynamic stability of pure crystalline UO_2(s) is very high with a Gibbs energy of formation of -1031.833 ± 1.004 $kJ \cdot mol^{-1}$ As already pointed out by the authors of the NEA-TDB compilation, the initial state of these pure crystalline solid phases is quite well defined. However, the final equilibrium stage in contact with near neutral solutions or groundwaters can be quite different. Many factors can be responsible for this apparent lack of thermodynamic consistency, including changes in the redox state of the surface, crystallinity effects and the formation of colloidal phases due to partial oversaturation. In this work, we will attempt to rationalise these observations in the light of the recent developments in the spectroscopic and microscopic observations of the equilibrated phases in order to explain the apparent inconsistency between the thermodynamic data and the measured dissolution behaviour in aqueous medium.