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Sonochemical Behaviour of Pu(III), Pu(IV), and Pu(VI) in Aqueous Nitric Solutions

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Reprocessing of spent nuclear fuel is currently carried out *via* the well-established PUREX process which is a hydrometallurgical treatment performed in nitric acid and based upon redox operations followed by selective solvent extraction of U and Pu.[1] In order to adapt this reprocessing technology to the future nuclear reactors but also to reply to the society concerns, new alternatives are nowadays under investigation to minimise the quantity of generated radioactive wastes, replace obsolete chemicals, increase safety and propose new routes of treatments also supposed resistant against proliferation. Sonochemistry uses the propagation of ultrasonic waves in liquid media to generate physico-chemical transformations in homogeneous solutions and heterogenous systems.[2] The effects generally attributed to ultrasound do not result from direct interactions of acoustic waves with molecules but rather from acoustic cavitation, which is the nucleation, growth and rapid implosive collapse of vapour filled micro-bubbles. At collapse, these bubbles lead to extreme transient conditions of several thousands of degrees and hundreds of atmospheres while keeping the solution at ambient temperature and pressure.

Sonication may therefore induce chemical transformations of the liquid medium involving redox reactions in solution.[2] For instance, sonolyse of pure water allows the accumulation of H_2O_2 in solution while the sonication of aqueous nitric solutions produces NO_x and HNO_2. In the presence of nitrous scavengers, H_2O_2 can also accumulate in nitric solutions with an increased formation yield when compared to pure water due to a different radical mechanism. Sonolysis of various Pu solutions was studied in diluted aqueous nitric solutions (20 kHz, Ar, V= 50 mL, 0.26-0.52 $W.mL^{-1}$) while varying the experimental conditions. The sonolysis of Pu(III) in 1 M HNO_3 allows to observe its oxidation to Pu(IV) resulting from HNO_2 generation by HNO_3 sonolysis. In these conditions, Pu(IV) cannot be reduced or oxidized to another specie. However, in the presence of anti-nitrous reagents, Pu(IV) is found to be reduced to Pu(III) with a rate increasing with the acoustic intensity. The extended sonication leads to an equilibrium state where Pu(III) and Pu(IV) coexist in various concentrations. This behaviour is attributed to the *in-situ* generation of H_2O_2 in agreement with what observed without ultrasound (Eq.1-2).[1]

$$2\ Pu^{4+} + H_2O_2 \rightarrow 2\ Pu^{3+} + O_2 + 2\ H^+ \qquad \text{(Eq. 1)}$$
$$2\ Pu^{3+} + H_2O_2 + 2\ H+ \rightarrow 2\ Pu^{4+} + 2\ H_2O \qquad \text{(Eq. 2)}$$

The concentration of Pu(VI) in aqueous nitric solutions in the presence of sulfamic acid was also found to decrease as a function of sonication time. The reduction allows to observe Pu(V) accumulation which disproportionate to Pu(IV) and Pu(VI). The reduction of Pu(VI) is however found to accelerate with sonication time which is explained by H_2O_2-reduction of Pu(IV) to Pu(III). Pu(III) may thereafter react with Pu(VI) in agreement with the well-known equilibrium Eq. 3 which explains the acceleration observed for the different species and allows the simultaneous observation of four different oxidation states of Pu in ~1 M HNO_3.

$$PuO_2^{2+} + Pu^{3+} \leftrightarrow PuO_2^{+} + Pu^{4+} \quad \text{(Eq. 3)}$$

[1] L. R. Morss, N. Edelstein and J. Fuger. *The Chemistry of the Actinide and Transactinide Elements*, Springer, Dordrecht, 2010.
[2] K. S. Suslick and D. J. Flannigan, *Ann. Rev. Phys. Chem.* 2008, **59**, 659.