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Title:

## Reductive Dissolution of PuO<sub>2</sub> and CeO<sub>2</sub> in the Presence of Ti Particles and Ultrasound Irradiation

**Abstract:** (Your abstract must use Normal style and must fit into the box. Do not enter author details)

Plutonium dioxide is a dense and hard material. It is particularly inert towards most chemical substances and is very refractive to dissolution especially when fired at high temperature. Acidic non complexing media cannot dissolve this material in agreement with the high positive free energy related to this process ( $\Delta_r G^\circ = 32\text{--}41 \text{ kJ}\cdot\text{mol}^{-1}$ ) [1,2]. The most famous media for dissolution of PuO<sub>2</sub> requires the use of catalytic amount of fluoride ions F<sup>-</sup> in boiling and concentrated nitric acid [3]. This complexing dissolution route however suffers from some drawbacks related to the relatively low rate of dissolution, the equipment corrosion, and the effluent management. Due to the existence of four relatively stable oxidation states of Pu in acidic media, redox dissolution of PuO<sub>2</sub> can be considered. Oxidative dissolution of PuO<sub>2</sub> can be enabled with oxidants having redox potentials higher than ~1.2 V/SHE for PuO<sub>2</sub><sup>2+</sup>/PuO<sub>2</sub> couple, or 1.4-1.6 V/SHE for PuO<sub>2</sub><sup>2+</sup>/PuO<sub>2</sub> couple [1-3]. Strong oxidant cations such as Ce(IV), Ag(II), or Am(V,VI) allow to successfully dissolve PuO<sub>2</sub> with the possibility of regenerating the oxidant ions with ozone or electrochemistry. Although very fast dissolutions are observed at almost room temperature for such processes, the overconsumption of oxidant ions in the presence of organic materials or fission products in the dissolver can be problematic. The reductive dissolution route can be performed with redox couples having potentials below ~0.5 V/SHE which may solve the corrosion problems and propose milder reaction conditions [1-3]. However, reported studies remain scarce and do not allow satisfactory dissolution kinetics and yields, in addition to the use of non-compatible reagents or solvents for nuclear industry.

In parallel, sonochemistry (i.e., chemical reaction driven by ultrasound) can be an efficient tool to accelerate processes and initiate in situ redox reactions. Recent studies demonstrated that the sonication of aqueous nitric solutions allows the control and stabilization of the oxidation state of actinide ions [4,5]. The effect observed in sonochemistry are not related to direct interactions of ultrasound waves with molecules but derive from acoustic cavitation, which is the nucleation, growth, and rapid implosive collapse of gas- and vapor-filled micro-bubbles. At collapse, extreme conditions reached inside the bubbles lead to the formation of excited and radical species that recombine and react in solution. In addition, physical phenomena accompanying these effects are able to activate extended solid surfaces through the erosion or fracture of grains, the increase of reactive surface area, and depassivation of surfaces. For instance, the oxidative dissolution of uranium carbide and metallic plutonium was found to be improved under ultrasound irradiation [4,6]. Furthermore, studies devoted to the dissolution of CeO<sub>2</sub> and PuO<sub>2</sub> in H<sub>2</sub>O<sub>2</sub> or HCOOH systems showed significant improvements under ultrasound irradiation [7]; however, reported kinetics were too low to consider any direct application.

In this context, the sonochemical and reductive dissolution of PuO<sub>2</sub> was investigated under relatively mild conditions. Due to its redox properties and crystallographic similarities, ceria was first investigated as an inactive surrogate for PuO<sub>2</sub>. After preliminary studies, “hot” experiments were carried out in Atalante facility (Marcoule) in a dedicated glove box where an ultrasonic reactor is implemented. Several oxides were prepared by thermal conversion of oxalate precursors and were rigorously characterized before experiments (SEM, XRD, BET, etc.). Dissolutions were followed by SEM and by UV-Vis spectrophotometry for PuO<sub>2</sub> and ICP-AES for CeO<sub>2</sub>. The quantitative dissolution of both oxides is observed at 33-35°C under ultrasound irradiation (20 kHz, Ar, 0.5-0.7 W.mL<sup>-1</sup>) in 0.5-1.0 M HNO<sub>3</sub> / 0.1 M [N<sub>2</sub>H<sub>5</sub>][NO<sub>3</sub>] / 1-3 M HCOOH in the presence of Ti particles inserted in the reactor as a generating source of reducing agents. Ultrasound allows the activation of Ti through the depassivation of its surface usually strongly non-reactive in nitric solutions. During sonication, dissolution rates and yields can be highly improved in the presence of dilute fluoride aliquots through the injection of NH<sub>4</sub>F or HF which allow the chemical depassivation of Ti surface. The rapid and complete dissolution of PuO<sub>2</sub> can be achieved under these conditions and is accompanied by Pu(III) accumulation in solution (Figure 1). Reductive dissolution in such dilute and mild conditions is a promising alternative towards the dissolution of this refractory oxide and the related reduced equipment corrosion and effluent generation.

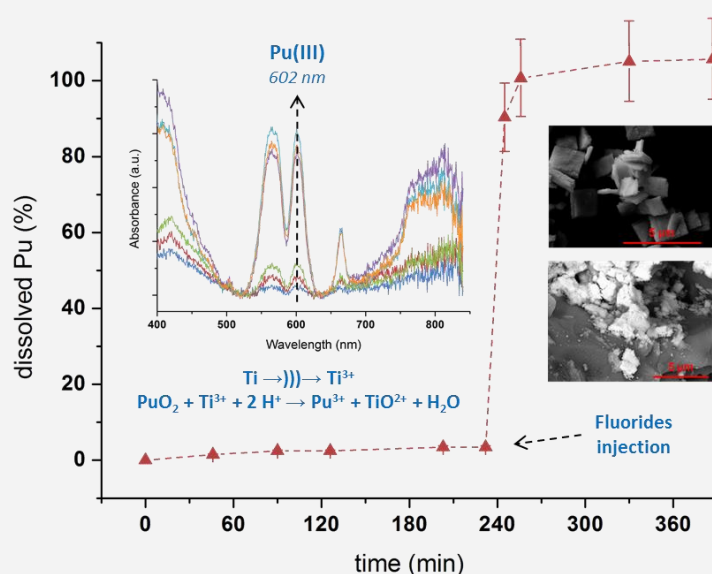


Figure 1: Dissolution kinetic of  $\text{PuO}_2$  ( $14 \text{ m}^2 \cdot \text{g}^{-1}$ , 150 mg) observed under ultrasound (20 kHz, Ar,  $0.45 \text{ W} \cdot \text{mL}^{-1}$ ) at  $35^\circ\text{C}$  in  $0.5 \text{ M HNO}_3 / 0.1 \text{ M } [\text{N}_2\text{H}_5][\text{NO}_3] / 2 \text{ M HCOOH}$  (50 mL) in the presence of Ti particles (140 mg, 325 mesh). Fluorides (50 mM) were injected at 230 min. Insets highlight the accumulation of Pu(III) in solution in such system with UV-Vis spectroscopy, the proposed dissolution mechanism, and SEM pictures of  $\text{PuO}_2$  ( $5 \text{ m}^2 \cdot \text{g}^{-1}$ ) before and after dissolution (bright colors: Pu, and dark colors: Ti) in similar conditions.

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