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## Sonochemical Redox Reactions of Pu(III) and Pu(IV) in Aqueous Nitric Solutions

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### Abstract

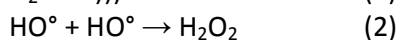
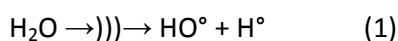
The behavior of Pu(IV) and Pu(III) was investigated in aqueous nitric solutions under ultrasound irradiation (Ar, 20 kHz). In the absence of anti-nitrous reagents, ultrasound has no effect toward Pu(IV) while Pu(III) can be rapidly oxidized to Pu(IV) due to the autocatalytic formation of HNO<sub>2</sub> induced by HNO<sub>3</sub> sonolysis. In the presence of anti-nitrous reagents (sulfamic acid or hydrazinium nitrate), Pu(IV) can be sonochemically reduced to Pu(III). The reduction follows a first order reaction law and leads to a steady state where Pu(IV) and Pu(III) coexist in solution. The reduction process is attributed to the sonochemical generation of H<sub>2</sub>O<sub>2</sub> in solution. The kinetics attributed to the reduction of Pu(IV) are however higher than those related to the formation of H<sub>2</sub>O<sub>2</sub> which, after several hypotheses, is explained by the sonochemical erosion of the titanium-based sonotrode. Titanium particles therefore generated can be solubilized under ultrasound and generate Ti(III) as an intermediate specie, a strong reducing agent able to react with Pu(IV).

## Introduction

H<sub>2</sub>O<sub>2</sub> has been an interesting and powerful salt free reagent for industry. It is cheap, available in large and pure quantities, and yields volatile oxidation species that do not interfere with final reaction products. Despite its radiolysis-induced occurrence, hydrogen peroxide has been considered as a chemical of paramount importance in actinide chemistry and nuclear processing because of its acido-basic, redox, and complexing properties.<sup>1, 2</sup> Besides its other advantages, using H<sub>2</sub>O<sub>2</sub> in large scale chemistry allows avoiding dilution of treated solutions which is particularly important in actinide chemistry where the control of hydrolysis and concentration of target elements is often challenging.<sup>1</sup> These attributes have been widely used for the purification, separation and oxidation state adjustment for several actinide elements including Pu, U, and Np.<sup>1-5</sup> Indeed, H<sub>2</sub>O<sub>2</sub> can be considered as both an oxidizing (1.77 V vs. SHE) and reducing (0.68 V vs. SHE) specie.

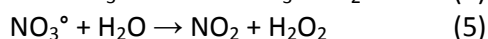
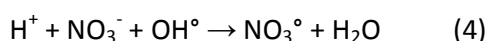
For instance, the addition of H<sub>2</sub>O<sub>2</sub> to Pu(VI) solutions has been routinely used to obtain and stabilize Pu(IV) aqueous nitric solutions prior to anion exchange separation and oxalate precipitation.<sup>1-4</sup> In nitric media, the reduction of Pu(VI) with H<sub>2</sub>O<sub>2</sub> occurs through Pu(V) formation which can also be thermodynamically reduced to Pu(IV). However, Pu(IV) accumulation is generated through Pu(V) dismutation because of its strong proton dependency and the higher kinetics required to break oxo bounds.<sup>1, 6, 7</sup> Hydrogen peroxide can also be used for the reduction of Pu(IV) leading to Pu(III) or to a steady-state composed of Pu(IV) and Pu(III) in various proportions.<sup>1, 3, 8, 9</sup> The shifting of this ratio is highly dependent upon the experimental conditions such as the temperature, acidity, counter-ion, or reactant concentrations. Pu(IV) reduction results from the formation of peroxy complexes that decompose in acidic media.<sup>2, 8-11</sup> Using these concentrations, plutonium may therefore be considered as a decomposition catalyst towards H<sub>2</sub>O<sub>2</sub>.

Ultrasound propagation in aqueous solutions offers the possibility of generating in-situ redox species in relatively mild conditions. This effect is not attributed to direct interactions of ultrasound waves with molecules, but rather from acoustic cavitation, which is the nucleation, growth, and rapid implosive collapse of vapour filled micro-bubbles.<sup>12-14</sup> At collapse, these micro-reactors may lead to the formation of chemical species able to react in the treated bulk solution. For instance, the sonolysis of pure water under Ar atmosphere causes the homolytic dissociation of H<sub>2</sub>O molecules according to the reactions (1-2) and generate radical species leading, after recombination, to the accumulation of hydrogen peroxide in the solution and release of molecular H<sub>2</sub> in the gaseous flow.<sup>14</sup> The formation rates follow zero-order kinetics and strongly depend upon the sonochemical conditions such as the ultrasound frequency, acoustic power, temperature, or gaseous atmosphere. Indeed, the 20 kHz sonication of pure water under Ar at 20°C leads to a sonochemical yield of H<sub>2</sub>O<sub>2</sub> formation of 0.06 μmol.kJ<sup>-1</sup> while 0.46 μmol.kJ<sup>-1</sup> are measured at 607 kHz using similar other conditions.<sup>15</sup>



In aqueous nitric solutions, the accumulation of H<sub>2</sub>O<sub>2</sub> is not observed due to the formation of nitrous acid which rapidly reacts with hydrogen peroxide (Eqn. 3).<sup>16</sup> The addition of anti-

nitrous reagents such as sulfamic acid, hydrazinium nitrate, or urea to the medium avoids the accumulation of  $\text{HNO}_2$  and therefore enables the presence of  $\text{H}_2\text{O}_2$  in solution. Previous investigations showed that the accumulation rate of hydrogen peroxide observed during the sonication of aqueous nitric solutions is higher than what observed in pure water.<sup>13, 17</sup> The formation rate observed for  $\text{H}_2\text{O}_2$  at 22 kHz and 24°C in 1 M  $\text{HNO}_3$  (in the presence of anti-nitrous reagent) was indeed found to be approximately 2.4 times higher than what observed in pure water with similar conditions. This phenomenon results from a different mechanism of formation for  $\text{H}_2\text{O}_2$  where  $\text{HO}^\circ$  reacts with nitrate ions to generate  $\text{NO}_3^\circ$  which leads to  $\text{H}_2\text{O}_2$  after hydrolysis (Eqn. 4-5).<sup>13, 17</sup> In this mechanism, only one hydroxyl radical is used to produce one hydrogen peroxide molecule whereas two hydroxyl radicals are required in pure water (Eqn. 2). Note that in heterogeneous systems, the implosive collapse of acoustic bubbles at the vicinity of extended surfaces is able to favour the fragmentation of particles and the erosion of surfaces. An increase of the mass transfer is also reported.<sup>14</sup>



The adjustment of the actinide oxidation state in recycling processes of spent nuclear fuel (e.g. PUREX) is important for their recovery and separation necessarily performed with very high yields.<sup>1-3, 18, 19</sup> The industrial addition of chemicals within recycling processing of nuclear fuel arouses the question of wastes and effluent management in addition to the already existing security limitations. High-power ultrasound offers the opportunity to generate in-situ redox species with controlled kinetics and therefore suggests the possible application of ultrasound in actinide chemistry.<sup>13</sup> Since the first investigations devoted to the chemical influence of ultrasound irradiation towards actinides, only a few studies have been reported in the literature. Mainly, the studies are dealing with the dissolution of oxides<sup>20-22</sup> and the valency control of actinide ions in aqueous solutions.<sup>23-26</sup> Note that more recently, the sonochemical excitation of uranyl ions has been demonstrated during sonoluminescence studies.<sup>27</sup> The aim of the present work was to evaluate the influence of ultrasound towards the redox behavior of Pu(IV) and Pu(III) in aqueous nitric solutions. For this study, sonochemical set-up have been developed in a “hot” glove box in Atalante facility (CEA Marcoule). The experiments were performed under Ar bubbling at 20 kHz at almost ambient temperature.

## Experimental Section

**Caution!** Pu is an  $\alpha$ -emitting element presenting serious health risks. Studies dealing with such an element require a careful handling coupled to appropriate infrastructures and trained workers.

### Materials

Stock solutions of Pu(IV) (~96.9%  $^{239}\text{Pu}$ ) in nitric acid were prepared by dissolving  $\text{PuO}_2$  powder in concentrated nitric acid with HF aliquots. The resulting solution was concentrated and purified in nitric media on a chromatographic column filled with a DOWEX anion exchange resin to remove impurities arising from Pu decay. Plutonium stock solution was then adjusted to its (IV) oxidation state using  $\text{H}_2\text{O}_2$  aliquots. Before investigations, the solution was characterized by determining the Pu concentration and the acidity of the solution (Radiometer titralab TIM865, electrode Radiometer XC161), and was stored in a lead castle until use. Used chemicals were all of analytical grade and were purchased from Sigma Aldrich. The various solutions were prepared using purified ultrapure water having a resistivity higher than  $18.2 \text{ M}\Omega\cdot\text{cm}$  ( $25^\circ\text{C}$ ).

### Sonochemical experiments

Active experiments were performed in ATALANTE facility (Marcoule) in a glove box devoted to investigations dealing with sonochemical reactions of actinide elements in various chemical systems. The negative pressure glove box is equipped with thermostated “cup horn” tight reactors (50 or 100 mL) connected to a Lauda E210 cryostat from outside the enclosure. Note that the cooling system is equipped with a heat exchanger avoiding a potential Pu contamination. A thermocouple inserted into the reactor allowed the control of the temperature which was maintained at  $25\text{-}30^\circ\text{C}$  during sonication experiments. Specific “non-active” experiments were performed at ICSM facility in a home-made reactor with an immersed probe already described in the literature.<sup>28, 29</sup> Sonochemical experiments were performed using 20 kHz ultrasonic processors purchased from Bioblock Scientific (Vibracell, 600 W, ATALANTE) and from Sonics & Materials (Vibracell, VCX 750, ICSM). The devices comprise a piezoelectric transducer coupled to a titanium horn of 1 (for the plunging probe), 7.9, or  $18.1 \text{ cm}^2$  (for the inversed “cup-horn” transducers).

The cells comprise Teflon rings ensuring reproducible airtight experiments. Sonochemical experiments were performed under Ar which was bubbling ( $100 \text{ mL}\cdot\text{min}^{-1}$ ) through the solution 20 min before starting sonication and was maintained during the whole experiments. In agreement with the literature, the sonochemical reaction rates are driven by the absorbed acoustic energy.<sup>30</sup> Therefore, to compare accurately the results obtained with the different geometries, the specific acoustic power ( $\text{W}\cdot\text{mL}^{-1}$ ) delivered to the solution was determined and assessed by the thermal probe method in agreement with the literature and the following equations (6-7):

$$P(W) = m C_p \left( \frac{dT}{dt} \right)_{t=0} \quad (6) \qquad P_{ac} (\text{W}\cdot\text{mL}^{-1}) = \frac{P}{V} \quad (7)$$

with,  $m$  the mass of the treated water,  $C_p$  the specific heat capacity of water at room temperature and pressure ( $4.18 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ), and  $V$  the volume of the sonicated solution (mL).

$\left(\frac{dT}{dt}\right)_{t=0}$  is the initial slope of the temperature variation of the solution against time under ultrasound irradiation. A detailed description of the geometric and calorimetric comparison between the different sonochemical reactor might be found in the literature for previous investigations.<sup>30</sup>

### UV-Vis spectroscopy

UV-Vis spectrometry analyses were directly recorded inside the glove box through optic fibers allowing the measurement of the solutions from 350 to 900 nm (Shimadzu UV3600 spectrometer). Pu(IV) was followed at ~476 nm ( $\epsilon = 73 \text{ cm}^{-1} \cdot \text{M}^{-1}$ ) while Pu(III) was followed at ~602 nm ( $\epsilon = 33 \text{ cm}^{-1} \cdot \text{M}^{-1}$ ). Concentration variations were determined by measuring the "peak-valley" difference in absorbance. The reported extinction and apparition rates for Pu(IV) and Pu(III) were established by tracing the initial slope of the corresponding kinetic curves for ca. 90 min and were given as  $W_0(-\text{Pu}^{\text{IV}})$  and  $W_0(\text{Pu}^{\text{III}})$ , respectively. Note that slight uncertainties may be pointed out for measurements due to the used optic fibers, particularly for Pu(III) which displays in addition a low extinction coefficient. The formation of hydrogen peroxide resulting from the homolytic dissociation of sonicated water molecules was measured by spectrophotometric method. The procedure consists in diluting aliquots of the sonicated media (pure water or aqueous nitric solution) with a solution made of  $2 \cdot 10^{-2} \text{ M}$   $\text{TiOSO}_4$  in  $0.5 \text{ M HNO}_3 - 0.01 \text{ M [N}_2\text{H}_5\text{][NO}_3\text{]}$ . The formation of a stable  $\text{Ti(IV) \cdot H}_2\text{O}_2$  complex is then followed at  $\lambda_{\text{max}} = 410 \text{ nm}$  ( $\epsilon = 730 \text{ cm}^{-1} \cdot \text{M}^{-1}$ ).<sup>31</sup> The detection limit of the method is  $\sim 3 \cdot 10^{-5} \text{ M}$ . The potential formation of hydroxylammonium nitrate during sonolysis was followed by colorimetric method using the ferrozine procedure. The operation consists in reducing  $\text{Fe(III)}$  with hydroxylamine to generate  $\text{Fe(II)}$  which react with the ferrozine salt (3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid disodium salt to produce a purple complex measured at  $\lambda_{\text{max}} = 560 \text{ nm}$  ( $\epsilon = 35000 \text{ cm}^{-1} \cdot \text{M}^{-1}$ ).<sup>31, 32</sup> The detection limit of the procedure is  $\sim 4 \cdot 10^{-6} \text{ M}$ .

### ICP-OES measurements

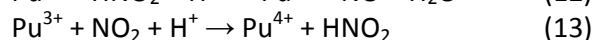
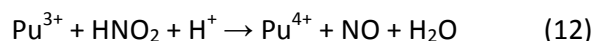
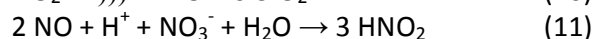
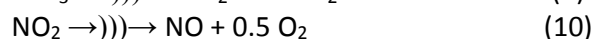
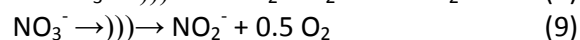
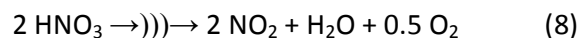
The concentration of titanium in inactive solutions was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Spectro Arcos device supplied by Spectro Analytical Instruments GmbH and equipped for axial plasma observation (for inactive experiments). Filtered aliquots ( $0.2 \mu\text{m}$  PTFE filters from VWR) of the treated solution were diluted with  $0.3 \text{ M HNO}_3$  to obtain a ~2% acidified solution and were analyzed against an external calibration curve prepared with certified Ti standard solutions (SCP Science, Courtaboeuf, France). The repeated measurements of these samples during analyses allowed determining standard deviations. The detection limit is ~0.1 ppm.

### MS measurements

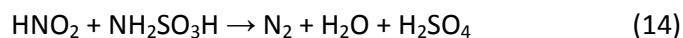
Mass spectrometry (MS) was used to evaluate the  $\text{H}_2$  formation during sonolysis in inactive conditions. Measurements were made with a quadrupole mass spectrometer (Prolab 300, Thermo Fisher). The water vapor potentially generated during sonolysis was trapped using  $3 \text{ \AA}$  molecular sieves (Sigma-Aldrich) prior to mass spectrometry experiments.

## Results and Discussion

In the absence of anti-nitrous reagents, preliminary investigations revealed that aqueous nitric solutions of Pu(IV) are chemically stable under ultrasound irradiation in agreement with the literature.<sup>24, 25, 31</sup> By contrast, the sonolysis of an equivalent Pu(III) solution leads to the rapid accumulation of Pu(IV). The reaction mechanism involves the *in-situ* generation of nitrous acid and NO<sub>x</sub> molecules from HNO<sub>3</sub> sonolysis.<sup>13, 16, 28</sup> It results from the thermolysis of non-dissociated HNO<sub>3</sub> molecules within the acoustic bubbles and nitrate ions at the liquid reaction zone surrounding the bubbles (Eqn. 8-9). Pu(III) oxidation with HNO<sub>2</sub> is rapid and autocatalytic as illustrated by the reactions (8-12). Secondary reactions may also occur with NO<sub>2</sub> in agreement with the reaction (13). In this system, the generation of HNO<sub>2</sub> avoids the accumulation of H<sub>2</sub>O<sub>2</sub> from water sonolysis (Eqn. 1-2) due to the rapid reaction of both species according to the reaction (3) already described in the introduction.<sup>13, 16</sup>



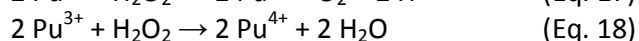
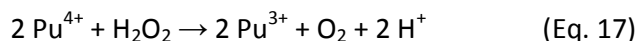
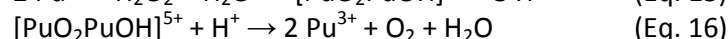
In the presence of 0.1 M sulfamic acid as an anti-nitrous reagent (Eqn. 14), the sonolysis of a Pu(IV) solution in 1 M HNO<sub>3</sub> leads to the significant decrease of Pu(IV) concentration followed at 476 nm. Simultaneously, the generation of Pu(III) is observed at 602 nm as illustrated by the selected UV-Vis spectra in the Figure 1. The evolution of the corresponding Pu concentrations measured in solution as a function of the sonication time are plotted on the Figure 2 for different acoustic powers. The observation of both Figures 1 and 2 evidences the simultaneous existence of Pu(III) and Pu(IV) in solution. For an acoustic power of 0.26 W.mL<sup>-1</sup>, the initial extinction and accumulation rates observed for Pu(IV) and Pu(III) respectively, are equivalent and linear:  $W_0(-\text{Pu}^{\text{IV}}) = 7 \mu\text{M} \cdot \text{min}^{-1}$  and  $W_0(\text{Pu}^{\text{III}}) = 8 \mu\text{M} \cdot \text{min}^{-1}$  (Figure 2.a.). When the acoustic power reaches 0.38 W.mL<sup>-1</sup>, the reaction rates are dramatically enhanced to  $W_0(-\text{Pu}^{\text{IV}}) = 17 \mu\text{M} \cdot \text{min}^{-1}$  and  $W_0(\text{Pu}^{\text{III}}) = 22 \mu\text{M} \cdot \text{min}^{-1}$ .



Although equivalents, Pu(IV) and Pu(III) rates are no more linear and are fitted with polynomial functions. Note that the slight rate difference observed between Pu(IV) and Pu(III) results from an uncertainty provided by the low extinction coefficient of Pu(III) coupled to the optic fibers used for UV-Vis measurements. When increasing again the delivered acoustic power to 0.45 W.mL<sup>-1</sup> (Figure 2.b.), the initial rate of extinction observed for Pu(IV) is about 20  $\mu\text{M} \cdot \text{min}^{-1}$  while the initial rate of accumulation reported for  $W_0(\text{Pu}^{\text{III}})$  reaches 22  $\mu\text{M} \cdot \text{min}^{-1}$ . In agreement with the Figure 2.a., this observation evidences the occurring relationship between the increases of Pu(IV) extinction rate and the delivered acoustic power. Note however that the reaction is not complete whatever the acoustic power and leads, for prolonged sonication, to a steady state where Pu(III) and Pu(IV) coexist in solution.

In these sonicated solutions, the presence of sulfamic acid involves the rapid scavenging of  $\text{HNO}_2$  formed during sonolysis according to the Eqn. (14) thus avoiding the achievement of the reaction (3).<sup>16</sup> This scavenger offers two advantages: it avoids the back-oxidation of  $\text{Pu(III)}$  with  $\text{HNO}_2$  when reduced, and allows in the meantime the quantitative accumulation of  $\text{H}_2\text{O}_2$  in nitric solution. However, in the presence of  $\text{Pu(IV)}$ ,  $\text{H}_2\text{O}_2$  was not observed most probably because of its consumption in  $\text{Pu}$  reduction process. In addition, other  $\text{Pu}$  valencies such as  $\text{Pu(VI)}$  or  $\text{Pu(V)}$  were not detected in the various sonicated solutions as evidenced by the Figure 1 and the total  $\text{Pu}$  content expressed by the green triangle plots on the Figure 2.b. (not shown in the Figure 2.a. for the clarity of the picture). In consequence,  $\text{Pu(III)}$  accumulation in the sonicated solutions can be attributed to the reduction of  $\text{Pu(IV)}$  resulting from the *in-situ* generation of hydrogen peroxide during sonication.

Without ultrasound, this redox reaction has been widely studied for  $\text{Pu}$  solution stabilization and/or purification in nitric media. The reaction is reversible and leads to a steady state which is strongly dependent upon reagent concentrations and acidity.<sup>1, 3, 7-9</sup> This steady state is supposed to result from the simultaneous back-oxidation of  $\text{Pu(III)}$  to  $\text{Pu(IV)}$  by hydrogen peroxide in agreement with the redox potentials of  $\text{Pu(IV)/Pu(III)}$  ( $E^\circ = 0.91 \text{ V vs. SHE}$ ) and  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  ( $E^\circ = 1.77 \text{ V vs. SHE}$ ) couples.<sup>11</sup> This assertion has been successfully verified in our system by sonicating a  $\text{Pu(III)}$  solution in an aqueous nitric solution in the presence of hydrazinium nitrate as anti-nitrous reagent (Figure S1, Supporting Information). It is also noteworthy that  $\text{Pu(III)}$  accumulation is supposed to occur from the decomposition of a soluble  $\text{Pu(IV)}$  peroxy complex which follows a first order rate law according to the reactions (15-16).<sup>2, 7-11</sup> These peroxides (usually observed at 495, 540, or 513 nm with relatively high extinction coefficient) were not detected in our solutions, probably because of their low amount and instability in acid media, which can be possibly intensified under ultrasound irradiation. The sonochemical reduction of  $\text{Pu(IV)}$  follows a first-order reaction law in agreement with the Figure S2, Supporting Information. In these conditions, the measured apparent rate constant is  $\sim 5.7 \cdot 10^{-3} \text{ min}^{-1}$ . In accordance with the previous observations and the literature, the overall reaction scheme of  $\text{Pu}$  ions in the sonicated system may be described by the equations (17-18).<sup>8-11</sup>



In order to compare  $\text{Pu}$  reduction with  $\text{H}_2\text{O}_2$  formation rates, similar experiments were performed in the absence of  $\text{Pu}$  ions to allow  $\text{H}_2\text{O}_2$  accumulation in solution. The determined sonochemical kinetics determined at similar experimental conditions are shown in the Table 1. In agreement with the above results and the literature,  $W_0(-\text{Pu}^{\text{IV}})$ ,  $W_0(\text{Pu}^{\text{III}})$  and  $W_0(\text{H}_2\text{O}_2)$  are increasing with the rising acoustic power  $P_{\text{ac}}$ .<sup>14</sup> As illustrated by the Figure 2,  $W_0(-\text{Pu}^{\text{IV}})$  and  $W_0(\text{Pu}^{\text{III}})$  exhibit equivalent rates whatever the experiment which emphasizes the relationship occurring between  $\text{Pu(IV)}$  and  $\text{Pu(III)}$ . However, these kinetics also reveal that  $\text{Pu(IV)}$  is reduced faster than  $\text{H}_2\text{O}_2$  is generated whatever  $P_{\text{ac}}$ . The stoichiometric equation (17) cannot completely explain the reduction of  $\text{Pu(IV)}$  in this system; the mechanism of reduction appears to exhibit a complementary reduction step not explained by the sole



reaction with  $\text{H}_2\text{O}_2$ . Note also that the calculated ratio  $W_0(-\text{Pu}^{\text{IV}})/W_0(\text{H}_2\text{O}_2)$  is increasing with the delivered acoustic power indicating that this phenomenon is influenced by the acoustic cavitation. By plotting  $W_0(-\text{Pu}^{\text{IV}})$  as a function of  $P_{ac}$ , a threshold value of  $0.17 \text{ W}\cdot\text{mL}^{-1}$  may be graphically established indicating the minimal acoustic power required to observe sonochemical Pu(IV) reduction (Figure S3, Supporting Information). This value is very close to the  $0.18 \text{ W}\cdot\text{mL}^{-1}$  threshold acoustic intensity ( $9 \text{ W}\cdot\text{cm}^{-2}$  for 50 mL with a  $1 \text{ cm}^2$  tip) reported in the literature when measuring  $\text{HO}^\circ$  generation under 22 kHz ultrasound.<sup>33</sup> This observation also emphasizes the already proposed reduction mechanism occurring with  $\text{H}_2\text{O}_2$ , a recombination product of  $\text{HO}^\circ$  radicals.

In order to evaluate the influence of the anti-nitrous reagent towards reduction kinetics, sulfamic acid was replaced by hydrazinium nitrate,  $[\text{N}_2\text{H}_5][\text{NO}_3]$ . The Figure 3.a. illustrates the evolution of selected UV-Vis absorption spectra for a sonicated solution (20 kHz, Ar,  $0.52 \text{ W}\cdot\text{mL}^{-1}$ ,  $V = 50 \text{ mL}$ ) of 5 mM Pu(IV) in 1 M  $\text{HNO}_3 - 0.1 \text{ M } [\text{N}_2\text{H}_5][\text{NO}_3]$ . The spectra evidence the simultaneous decrease of Pu(IV) concentration at 476 nm coupled to the growth of Pu(III) at 602 nm in agreement with the Figures 1 and 2. The corresponding plotted data for Pu concentrations in this system are illustrated on the Figure 3.b. In agreement with the results reported in sulfamic media (Figure 2), the initial rates of reduction for Pu(IV) and accumulation for Pu(III) are equivalent ( $27 \mu\text{M}\cdot\text{min}^{-1}$ ). The kinetic curves exhibit a polynomial behavior with a first reaction order (apparent rate constant of  $7.5 \cdot 10^{-3} \text{ min}^{-1}$ ) leading to a steady state shifted toward Pu(III) formation (Supporting Information, Figure S4). Analyses evidenced the absence of hydrogen peroxide in solution during sonolysis which emphasize again the predominant role of  $\text{H}_2\text{O}_2$  in Pu(IV) reduction. Furthermore, the total concentration of plutonium is consistent during sonolysis, indicating that no extra valency state of Pu is generated during Pu(IV) reduction.

The initial rates observed for Pu(IV) reduction and Pu(III) accumulation however present higher values than what observed in the presence of sulfamic acid. This phenomenon results from the presence of hydrazinium nitrate which is known to be a good reducing agent for Pu(IV).<sup>1, 34</sup> The reaction (19) characterizes the limiting occurring process with excess of hydrazinium nitrate. The reduction rate of Pu(IV) attributed to the presence of  $[\text{N}_2\text{H}_5][\text{NO}_3]$  can be independently measured in order to evaluate the kinetics only attributed to ultrasound in this system in agreement with the following formula (20):



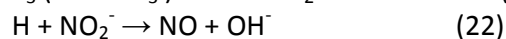
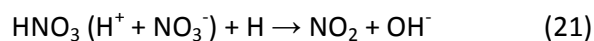
$$W_0(-\text{Pu}^{\text{IV}})_{\text{US}} = W_0(-\text{Pu}^{\text{IV}})_{\text{US+NH}} - W_0(-\text{Pu}^{\text{IV}})_{\text{NH}} \quad (20)$$

Pu(IV) reduction was therefore studied in 1 M  $\text{HNO}_3 - 0.1 \text{ M } [\text{N}_2\text{H}_5][\text{NO}_3]$  in silent conditions under stirring with other experimental conditions being equal. The Figure 4 illustrates the various kinetics observed for Pu(IV) in the presence and absence of ultrasound; the same picture completed with Pu(III) data may be found in the Supporting Information, Figure S5. The initial rate of reduction for Pu(IV) attributed to the sole presence of hydrazinium nitrate (Eq. 7) reaches  $6 \mu\text{M}\cdot\text{min}^{-1}$  (and  $7 \mu\text{M}\cdot\text{min}^{-1}$  for Pu(III) accumulation). The reduction with  $[\text{N}_2\text{H}_5][\text{NO}_3]$  follows a first order reaction law with an apparent rate constant of  $\sim 1.3 \cdot 10^{-3} \text{ min}^{-1}$ . By subtracting the corresponding reduction curve to the one measured during the sonolysis of the same solution ( $W_0(-\text{Pu}^{\text{IV}})_{\text{US+NH}}$ ), Pu(IV) reduction attributed to  $\text{H}_2\text{O}_2$  generation can be deduced (red curve) and the initial rate of reduction can be measured for

this system:  $W_0(-\text{Pu}^{\text{IV}})_{\text{US}} = 22 \mu\text{M}\cdot\text{min}^{-1}$ . The deduced reduction rate agrees with previous observations (Figure 2) and can be compared to  $W_0(\text{H}_2\text{O}_2)$  observed in the same conditions (i.e., in the absence of Pu in solution in order to accumulate  $\text{H}_2\text{O}_2$ ). In agreement with what observed in the presence of sulfamic acid, Pu(IV) reduction occurs faster than  $\text{H}_2\text{O}_2$  is produced (a formation rate of  $5.3 \mu\text{M}\cdot\text{min}^{-1}$  was observed under these conditions); the observed kinetics cannot be only explained by the stoichiometry of the reactions (15-16). As it was shown above in the presence of sulfamic acid, the reaction assumes an additional reduction step not explained by the sole generation of hydrogen peroxide.

Note that redox reactions involving plutonium ions and sonochemically-produced radical species ( $\text{HO}^\circ$ ,  $\text{NO}_3^\circ$ ,  $\text{H}^\circ$ , etc.) could also be considered. However, these radicals mostly recombine inside the bubble and their reactions with species from the bulk or the bubble interface are considered lower and limited by the fact that ions cannot diffuse inside the bubble. On the other hand, the quantity of radicals diffusing from the bubble to the solution is known to be very small; the contribution of direct radical mechanisms is therefore expected negligible in comparison to the reactions occurring with radical recombination products such as  $\text{H}_2\text{O}_2$  or  $\text{H}_2$ .

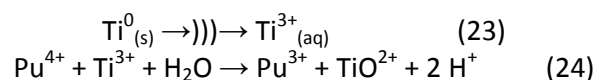
Nevertheless, several hypotheses were proposed to explain the kinetic discrepancies observed during the sonochemical reduction of Pu(IV) in comparison to the related accumulation rate of  $\text{H}_2\text{O}_2$ . For instance, H atom and molecular  $\text{H}_2$  are good reducing agent that can be generated from aqueous solution sonolyses. On-line mass spectrometry was used to determine the continuous generation of  $\text{H}_2$  in solution during sonication. Experiments revealed that the formation of  $\text{H}_2$  in 1 M  $\text{HNO}_3$  (with or without anti-nitrous reagent) was even lower than it is generally reported in pure water sonolysis using the same other conditions. Nitrates and nitrites are indeed known to be very good H atom scavengers therefore avoiding the generation of molecular  $\text{H}_2$  in this sonicated system in agreement with the equation (21-22).<sup>13, 17, 35, 36</sup>



Hydroxylammonium nitrate is known to be an effective reducing agent toward Pu(IV). In principle, the sonolysis of nitric acid in the presence of anti-nitrous reagents used in this work could lead to the formation of hydroxylamine intermediate as it is shown in the Supporting Information. UV-Vis spectrophotometry and ion chromatography were used to determine the possible generation of this specie during sonolyses. Both techniques revealed the absence of hydroxylamine in the sonicated solutions.

Finally, investigations showed that the prolonged sonication of Pu solution involved the significant accumulation of visible grey Ti particles in solution. This effect results from the implosive collapse of acoustic bubbles at the vicinity of extended solid surfaces.<sup>14, 37, 38</sup> At collapse, concerted micro-jets and shock waves provoke the erosion of surfaces. The following depassivation and fragmentation of particles enhanced by the increase of the mass transfer may favors solubilization. Sonotrode tips made out of titanium alloy may therefore erode and liberate Ti particles in solution. After 0.2  $\mu\text{m}$  filtration, ICP-AES evidenced the presence of Ti in sampled solution as a function of the sonication time (Figure 5). In this

system, Ti accumulation rate was found to have the same magnitude order than the one observed during Pu(IV) reduction. Considering that  $Ti^0$  dissolution in  $HNO_3$  medium involves the formation of Ti(III) unstable intermediate and  $TiO^{2+}$  as a final product, one can assume that at least some part of Ti(III) ( $E \sim 0$  V vs. SHE) may participate in Pu(IV) reduction. This specie has been already used for  $PuO_2$  reductive dissolution in non-nitric medium.<sup>22, 39</sup> The additional reduction kinetics observed in the sonicated Pu solution may in consequence be attributed to the presence of Ti particles in solution in agreement with the following reaction scheme (23-24).



Titanium and its alloys are famous for their high corrosion resistance because of the formation of an insoluble oxide layer on their surface. Ti particles observed using our conditions should be highly passivated in nitric solution; however, the application of ultrasound irradiation significantly contributes in the depassivation and/or solubilization of these particles. Note also in the Figure 5 the lower accumulation rate observed for Ti in 1 M  $HNO_3$  in the presence of sulfamic acid. This probably results from a better solubilization of Ti particles in the presence of nitrous acid and  $NO_x$  generated under ultrasound. The influence of Titanium in this chemical system was also emphasized by preparing filtrated and non-filtrated aliquots of Pu solutions after prolonged Pu sonolyses. The comparison of these aliquots after several days showed the dramatic decrease of Pu(IV) concentration and increase of Pu(III) for the non-filtrated solution while the filtrated aliquot evolved only slightly with time (this slight variation may be attributed to the presence of smaller Ti particles not retained on the filter). This observation indicates that Ti particles may also directly participate in Pu(IV) reduction probably via the reaction at the interface.

## Conclusion

This study demonstrates the potential of ultrasound to control the oxidation state of actinides in solution. The sonochemical reduction of Pu(IV) to Pu(III) can be observed in diluted nitric solutions in the presence of anti-nitrous reagents. Reduction reaction occurs through the in-situ generation of H<sub>2</sub>O<sub>2</sub> according to a first order reaction law and leads to a steady state where Pu(IV) and Pu(III) coexist in solution. The initial reaction rate is highly function of the delivered acoustic power and the observed kinetics discrepancies can be attributed to the accumulation and subsequent solubilization of Ti particles produced from the ultrasonic probe erosion. Sonochemistry offers the opportunity to generate *in situ* redox species without adding any chemicals which could be appropriate in nuclear processing where diminishing the quantity of waste and effluents is of particular interest. The yields reported in this study should be dramatically increased in future investigations by adjusting the saturating gas and ultrasonic frequency. Once adapted to the large scale, ultrasound irradiation could offer a suitable kinetic control for Pu stabilization thus avoiding the formation of peroxy-complexes sometimes encountered in nuclear processing.

## Acknowledgements

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Table 1: Comparison of the sonochemical kinetics (Ar, 20 kHz, V= 50 mL, 0.26-0.45 W.mL<sup>-1</sup>) observed in 1 M HNO<sub>3</sub> - 0.1 M NH<sub>2</sub>SO<sub>3</sub>H for Pu(IV) reduction and H<sub>2</sub>O<sub>2</sub> accumulation

$P_{ac}$ (W.mL <sup>-1</sup> )	$W_0(H_2O_2)$ ( $\mu M.min^{-1}$ )	$W_0(-Pu^{IV})$ ( $\mu M.min^{-1}$ )	$W_0(Pu^{III})$ ( $\mu M.min^{-1}$ )	$W_0(-Pu^{IV})/W_0(H_2O_2)$ -
0.26	2.7	7	8	2,6
0.38	5.5	17	22*	3,1
0.45	6.3	22	22	3,5

\*Note that the precision for this experiment was particularly low and results from the optic fibers and the low molar extinction coefficient of Pu(III). This problem can be observed on the Figure 2.a. only.

Figure 1: UV-Vis absorption spectra observed during the sonolysis (20 kHz, Ar, 25-29°C) of Pu(IV) in 1 M HNO<sub>3</sub> in the presence of 0.1 M NH<sub>2</sub>SO<sub>3</sub>H.

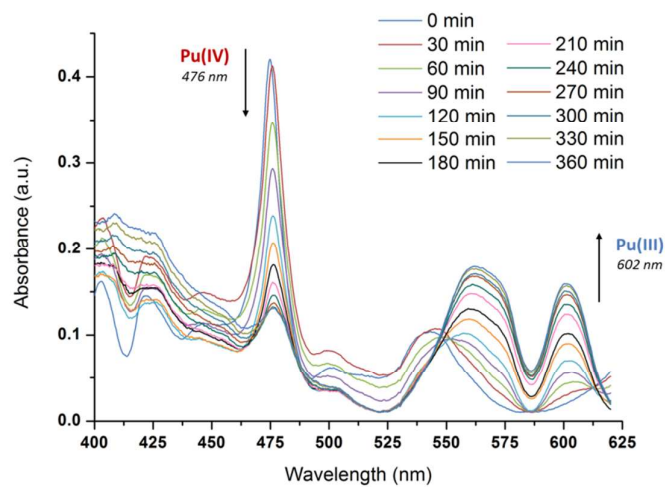


Figure 2: Sonolysis (20 kHz, Ar, 25-29°C) of Pu(IV) in 1 M HNO<sub>3</sub> in the presence of 0.1 M NH<sub>2</sub>SO<sub>3</sub>H at (a.) 0.26, 0.38, and (b.) 0.45 W.mL<sup>-1</sup>.

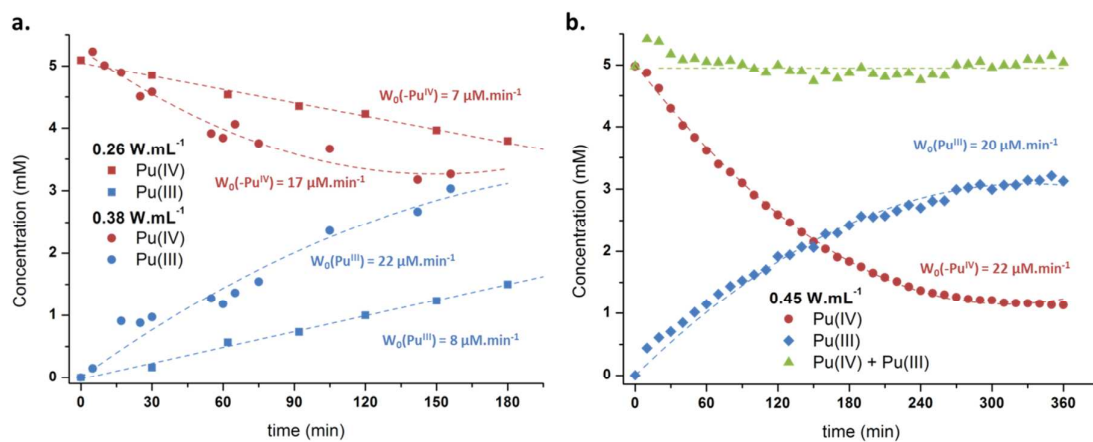




Figure 3: (a.) UV-vis absorption spectra and (b.) the corresponding plotted data observed during the sonochemical (20 kHz, Ar, 26°C) reduction of Pu(IV) in 1 M HNO<sub>3</sub> in the presence of 0.1 M [N<sub>2</sub>H<sub>5</sub>][NO<sub>3</sub>] at 0.52 W.mL<sup>-1</sup>.

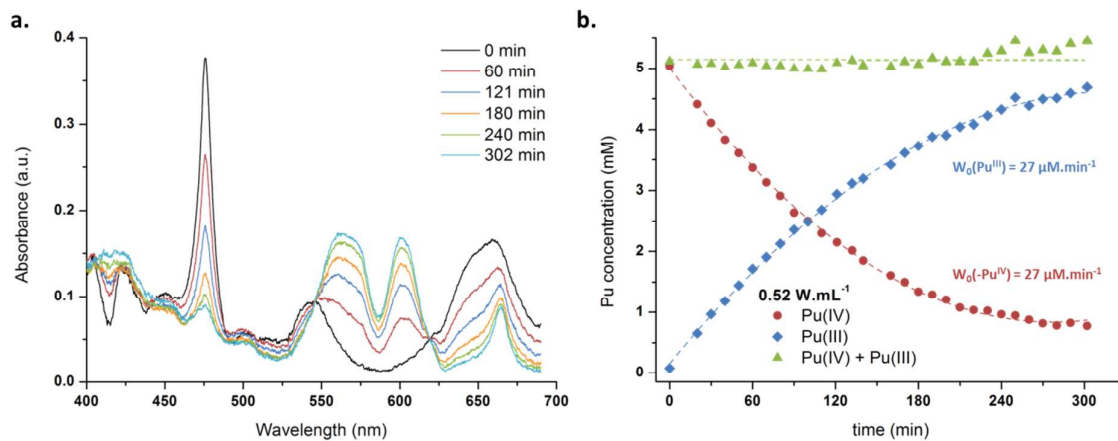


Figure 4: Reduction of Pu(IV) under stirring or ultrasound (20 kHz, Ar, 0.52 W.mL<sup>-1</sup>, 26°C) in 1 M HNO<sub>3</sub> - 0.1 M [N<sub>2</sub>H<sub>5</sub>][NO<sub>3</sub>].

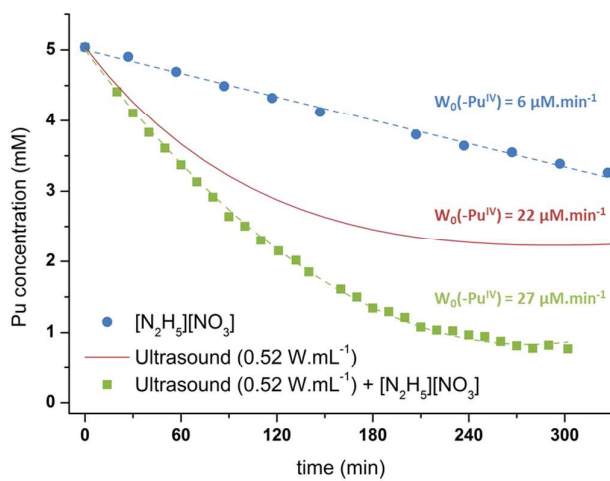


Figure 5: Titanium (mM) determination (ICP-AES) as a function of sonication time in 1 M  $\text{HNO}_3$  with or without 0.1 M  $\text{NH}_2\text{SO}_3\text{H}$ . The black dashed lines are the linear fit of the observed data and the surrounding lines are assigned to their relative 0.95 percentile confidence limits. The insert is a picture of a titanium tip before and after several hours (8-10 h) of sonication in aqueous solution.

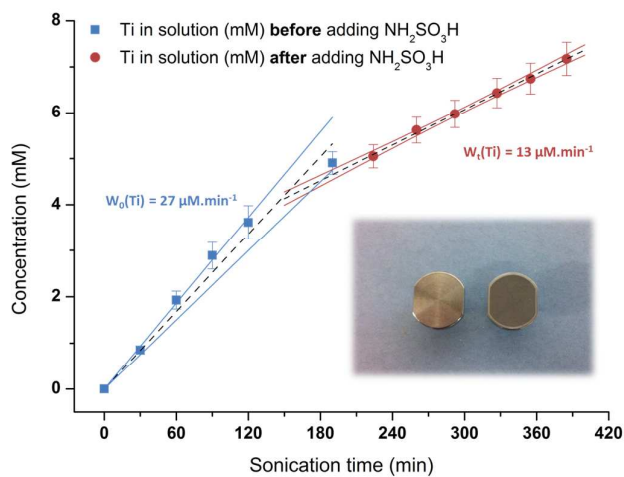
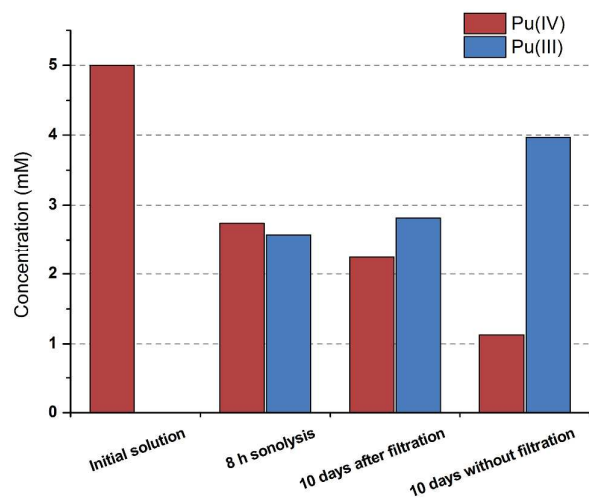


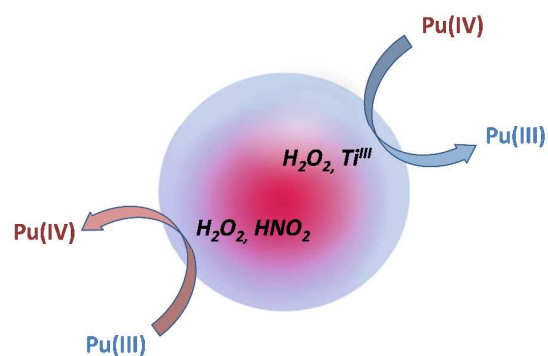
Figure 6: Evolution of Pu(III)/Pu(IV) ratio in filtrated and non-filtrated solution after sonolysis (20 kHz, Ar, 1 M HNO<sub>3</sub> - 0.1 M NH<sub>2</sub>SO<sub>3</sub>H).



## TOC Graphic

**Sonochemical Redox Reactions of Pu(III) and Pu(IV) in Aqueous Nitric Solutions**

Matthieu Virost †, Laurent Venault ‡, Philippe Moisy ‡, Sergey I. Nikitenko†



The 20 kHz sonication of aqueous nitric solutions generates active species which can further react with  $Pu(IV)$  and  $Pu(III)$  ions