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# Pulse radiolysis study on the reactivity of $\text{NO}_3^\bullet$ radical toward Uranous (IV), hydrazinium nitrate and hydroxyl ammonium nitrate at room temperature and at 45 °C

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## ABSTRACT

Concentrated nitric acid solutions subjected to radiation produce radicals of extreme importance in the reprocessing of spent nuclear fuel. Knowledge of the different rate constants of the reactions involved in this chemistry is needed to improve the efficiency of the process and to define safe operating practices. Pulse radiolysis measurements are performed to find the rate constant of the reaction between  $\text{NO}_3^\bullet$  radicals and U(IV) in highly concentrated nitrate solution. The optimal stabilization conditions toward thermal oxidation are defined for the considered solutions at room temperature and at 45°C by adding the anti-nitrous agents such as hydrazinium nitrate (HN) and hydroxyl ammonium nitrate (HAN). The decay of the  $\text{NO}_3^\bullet$  radical is monitored and its reaction rates with HN, HAN and U(IV) are found to be  $1.3 \times 10^5$ ,  $1.5 \times 10^7$  and  $1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at room temperature. The latter value is more than 10 times lower than the one currently used in numerical codes for simulation of the long-term radiolytic degradation associated with the reprocessing and storage of spent nuclear waste. At 45°C, conditions similar to the reprocessing of spent fuel, the values of the rate constants of  $\text{NO}_3^\bullet$  radical toward HN, HAN and U(IV) increase and are found to be  $2.6 \times 10^5$ ,  $2.9 \times 10^7$  and  $9.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

## Introduction

An increasing demand of energy in the XXI<sup>st</sup> century, combined with societal demands to preserve the livability of planet earth emphasizes the need for a consciously responsible energetic transition. Several countries have committed towards an enhanced deployment of renewable energy in order to reduce or eliminate the burning of fossil fuel for electricity, heat and transportation as the primary source of green gas emissions. As reform of the energy market is imminent, the nuclear energy still plays an important role as a virtually  $\text{CO}_2$  benign source, providing access to clean, reliable and affordable energy, currently supplying 75% of the total electricity in France. Currently, 30 countries use nuclear power and about the same number are considering, planning or

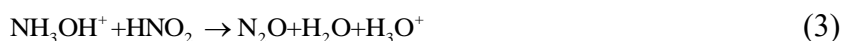
actively working on including it in their energy mix, with an International Atomic Energy Agency (IAEA), Organization for Economic Cooperation and Development (OECD), International Energy Agency (IEA) and World Nuclear Association (WNA) projected global nuclear power capacity growth from its current level of 381.7 GW(e) to 600-700 GW(e) by 2030. Through the energy reform debate, and concerns over the risks associated with nuclear energy, constant efforts are made in the industry in order to guarantee safety, long functioning and performance of nuclear power plants. The major area of investigations, for more than a half of century, has been the separation and recovery of actinides from the spent nuclear fuel. These developments will open the way for differentiated management modes, which will contribute ultimately to downsizing the waste volume and reduce its intrinsic radiotoxicity levels.<sup>1</sup> The preferred industrial reprocessing technology is the hydrometallurgical one, with the PUREX process at its core, a liquid-liquid extraction processes, allowing the recovery and recycling of major actinides.<sup>2,3</sup> The MO<sub>x</sub> (mixed oxide (U-Pu)O<sub>2</sub>) fuel fabrication earned first place in the uranium and plutonium recycling industry, with a recycling success rate of 99.9%.<sup>4</sup>

The first step of PUREX processes consists of spent nuclear fuel dissolution in nitric acid, with subsequent uranium U(VI) (U<sup>VI</sup>O<sub>2</sub><sup>2+</sup>) and plutonium Pu(IV) (and a low fraction of Pu(VI)) co-extraction into an organic phase, usually consisting of diluted tri-n-butyl-phosphate (TBP). Subsequently, Pu partitioning into an aqueous stream is performed by reducing Pu(IV) to Pu(III) and purifying it. The chemical separation steps are carried out at room temperature or at 45°C, depending on the equipment used. The use of nitric acid as a reaction medium, for all nuclear fuel treatment operations is based on its redox, acido-basic and complexing properties.<sup>5</sup> Due to the oxidation of U<sup>IV</sup>O<sub>2</sub> to U<sup>VI</sup>O<sub>2</sub><sup>2+</sup>, the instability of HNO<sub>3</sub> towards temperature and radiation,<sup>6,7</sup> from the first step of dissolution of fuel elements, accumulation of NO<sub>2</sub>, HNO<sub>2</sub>, and NO in solution (NO<sub>x</sub>) can occur, that affects the redox potential of the aqueous media.<sup>8</sup> Part of the HNO<sub>2</sub> produced can escape as NO<sub>x</sub> gases from the liquid, part is extracted into the TBP organic phase and part remains in the aqueous phase. Uranous (IV) nitrate aqueous solution that is used as a reductant of Pu(IV) to Pu(III) can also be oxidized into U(VI) in the presence of HNO<sub>2</sub>.<sup>9</sup> The U(VI)/U(IV) couple (~0.33 V/SHE in HClO<sub>4</sub> 1 M<sup>10</sup>) is smaller than the one corresponding to HNO<sub>2</sub> in nitric acid media (E°(HNO<sub>2</sub>/NO) = 0.996 V/SHE<sup>11</sup>), rendering U(IV) unstable. Pu(III), also being an unstable species, can rapidly be re-oxidized into Pu(IV) in the presence of nitrous acid, leading to partitioning failure. This is a self-catalyzing reaction, as it leads to the production of more HNO<sub>2</sub> than it consumes.<sup>12</sup>

The most commonly used anti-nitrous agent in the PUREX process is hydrazinium nitrate (HN), as it is capable of rapidly destroying the nitrous acid in aqueous solution. In acidic media, hydrazinium exists under two protonated forms (pK<sub>a1</sub> = 7.9<sup>13-15</sup> 8.1<sup>16</sup> 8.23<sup>17</sup> and pK<sub>a2</sub> = -1<sup>18</sup>): N<sub>2</sub>H<sub>5</sub><sup>+</sup> and N<sub>2</sub>H<sub>6</sub><sup>2+</sup>.<sup>19</sup> The interaction between nitrous acid and hydrazinium leads to the formation of hydrazoic acid as chemical intermediate.<sup>20-23</sup>



Due to its Pu(IV) to Pu(III) reducing capacity and scavenging properties of nitrous acid and prevention of back-oxidation of Pu(III), hydroxyl ammonium nitrate (HAN) was proposed as a reducing agent in the PUREX process.<sup>24-27</sup> HAN exists in HNO<sub>3</sub> under its protonated form NH<sub>3</sub>OH<sup>+</sup> (pK<sub>a1</sub> = 5.96<sup>28</sup>). However, the destruction of HNO<sub>2</sub> occurs much slower than in the presence of HN, according to reaction (3).<sup>23,29,30</sup> In 1970, Walser et al<sup>21</sup> showed the successful use of a hydroxyl ammonium nitrate-hydrazinium mixture as reducing agent to obtain an efficient U decontamination, Pu and Np recovery in the PUREX based process. The use of hydroxyl ammonium nitrate reduces the quantity of hydrazinium converted into hydrazoic acid from 5% to 30%, avoiding addition of supplemental chemical reductants such as U(IV) (or Fe(II)) to the process.



In sufficiently high concentrations of nitric acid an autocatalytic reaction can occur, which can lead to the formation of HNO<sub>2</sub>, rather than its destruction:<sup>31</sup>



Borderline conditions for the transition of HNA from a nitrous acid scavenger to a species responsible for the production of HNO<sub>2</sub> have been determined: a [HNO<sub>3</sub>] and temperature increase and a decrease of [HAN], all favor reaction (4).<sup>32,31</sup>

The study of the effects of ionizing radiation on acidic solutions containing actinides provides information on their redox behaviors and their reactivities towards the free radicals issued from the radiolysis of HNO<sub>3</sub>. It is therefore of extreme importance to fully understand and develop numerical models for the chemical process of actinides during the nuclear fuel reprocessing, and to do so, kinetic information on the reaction rates is needed. A few radiolytic models for U, Np, Pu and Am ions in concentrated nitric and perchloric acid solutions have already been proposed,<sup>33-36</sup> but questions still remain on the reaction rates involved in the process. Addition of stabilizing agents into the HNO<sub>3</sub> solutions can prevent U(IV) and Pu(III) oxidation by nitrous acid with an autocatalytic mechanism, and avoid partition failure in the PUREX process. Therefore the oxidation of U(IV) and Pu(III) by HNO<sub>3</sub>/HNO<sub>2</sub> mixture is of extreme interest,<sup>37-43</sup> not only for maintaining and optimizing the currently operating process but also for developing more efficient methods. Predicting and controlling the reaction pathways of U(IV), HAN and HN in the PUREX process is important for defining safe operating conditions for the use and storage of these compounds, for improving the product separation and recovery and waste management process.

The radiolytic behavior of HNO<sub>3</sub> solutions<sup>44-46,6,47-53</sup> has been fully characterized, and the nitrate radicals (NO<sub>3</sub><sup>•</sup>) formation mechanism has been elucidated.<sup>54,55,52,56</sup> The nitrate radicals (NO<sub>3</sub><sup>•</sup>) are used in most investigations as a probe to monitor the radiation-induced changes in HNO<sub>3</sub> solutions,<sup>57,46,49,58,54,50,55,59,56</sup> as they are known to be key radiolytic intermediates and drivers of chemical changes through the formation of secondary radiolytic products or through the oxidation of important metal ions. The three reactions responsible for the production of nitrate radicals are presented in Table 1: the reaction between <sup>•</sup>OH radicals and undissociated HNO<sub>3</sub> molecules (14),<sup>49,60</sup> the direct action of ionizing radiation on NO<sub>3</sub><sup>-</sup> ions (6) and HNO<sub>3</sub>

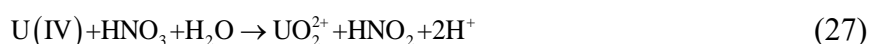
molecules<sup>61,46</sup> and oxidation of NO<sub>3</sub><sup>-</sup> ions and undissociated acid molecules by the primary water cation radical H<sub>2</sub>O<sup>•+</sup> (11).<sup>58</sup>

**Table 1.** Main reactions occurring in the radiolysis of aqueous solutions of HNO<sub>3</sub> containing uranium, and associated reaction rate constants in M<sup>-1</sup> s<sup>-1</sup>.

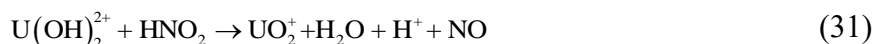
$\text{NO}_3^- \rightarrow \text{NO}_3^+ \rightarrow \text{NO}_2^- + \text{O}$		(5)
$\text{NO}_3^- \xrightarrow{[2]} \text{NO}_3^+ \rightarrow \text{NO}_3^+ + \text{e}^-$		(6)
$\text{NO}_3^- + \text{e}_{\text{pre}}^- \rightarrow \text{NO}_3^{2-}$	$4.5 \times 10^{12};$ <sup>62</sup>	(7)
$\text{NO}_3^- + \text{e}_{\text{sol}}^- \rightarrow \text{NO}_3^{2-}$	$9.7 \times 10^9;$ <sup>63</sup>	(8)
$\text{NO}_3^- + \text{H}^+ \rightarrow \text{HNO}_3$	$1 \times 10^7;$ <sup>64</sup>	(9)
$\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H}_3\text{O}^+$	$\sim 10^{13};$ <sup>65,66</sup>	(10)
$\text{H}_2\text{O}^{•+} + \text{NO}_3^- \rightarrow \text{NO}_3^+ + \text{H}_2\text{O}$		(11)
$\text{H}^+ + \text{e}_{\text{pre}}^- \rightarrow \text{H}^+$		(12)
$\text{H}^+ + \text{e}_{\text{sol}}^- \rightarrow \text{H}^+$	$2.3 \times 10^{10};$ <sup>67</sup>	(13)
	$1.4 \times 10^7;$ <sup>54</sup>	
	$9.03 \times 10^7;$ <sup>49,68</sup>	
$\text{OH}^+ + \text{HNO}_3 \rightarrow \text{NO}_3^+ + \text{H}_2\text{O}$	$5.3 \times 10^7;$ <sup>56,69</sup>	(14)
	$8.6 \times 10^7;$ <sup>70</sup>	
$\text{NO}_3^+ + \cdot\text{OH} \rightarrow \text{NO}_2^+ + \text{HO}_2^+$		(15)
$2\text{UO}_2^+ + 4\text{H}^+ \rightarrow \text{UO}_2^{2+} + \text{U}^{4+} + 2\text{H}_2\text{O}$	$3 \times 10^3;$ <sup>71</sup>	(16)
$\text{UO}_2^{2+} + \text{e}_{\text{aq}}^- \rightarrow \text{UO}_2^+$	$1.7 \times 10^{10};$ <sup>63</sup>	(17)
$\text{UO}_2^{2+} + \text{H}^+ \rightarrow \text{UO}_2^+ + \text{H}^+$	$4.1 \times 10^7;$ <sup>64,72</sup>	(18)
$\text{U}^{4+} + \text{H}^+ \rightarrow \text{U}^{3+} + \text{H}^+$	$1 \times 10^6;$ <sup>64,72</sup>	(19)
$\text{UO}_2^+ + \text{OH}^+ \rightarrow \text{UO}_2^{2+} + \text{OH}^-$	$4 \times 10^9;$ <sup>64,72</sup>	(20)
$\text{UO}_2^+ + \text{NO}_3^+ \rightarrow \text{UO}_2^{2+} + \text{NO}_3^-$	$2 \times 10^4;$ <sup>69</sup>	(21)
$\text{UO}_2^+ + \text{NO}_2^+ \rightarrow \text{UO}_2^{2+} + \text{NO}_2^-$	$1 \times 10^3;$ <sup>67,69</sup>	(22)
$\text{UO}_2^+ + \text{HNO}_2 \rightarrow \text{UO}_2^{2+} + \text{HNO}_2^-$	$8.6 \times 10^8;$ <sup>71</sup>	(23)

$U^{4+} + NO_3^{\bullet} \rightarrow UO_2^+ + NO_3^-$	$2 \times 10^7; ([H^+] = 1 M)^{71}$	(24)
$U^{4+} + NO_2^{\bullet} \rightarrow UO_2^+ + NO_2^-$	$1 \times 10^2;^{71}$	(25)
$U^{4+} + H_2O_2 \rightarrow UO_2^+ + OH^{\bullet} + OH^-$	$11;^{71,72}$	(26)

The oxidation of U(IV) in nitric acid exhibits an initial induction period, in which oxidation of HNO<sub>3</sub> occurs producing HNO<sub>2</sub>, followed by an autocatalytic reaction, in which U(IV) is oxidized by the resulting HNO<sub>2</sub>.<sup>38,73,74</sup>



The activation energies of reactions (27) and (28) are  $E_{27} = 103 \pm 15$  and  $E_{28} = 93 \pm 5$  kJ mol<sup>-1</sup>.<sup>73,75</sup> The induction period duration is reduced with increasing acidities,<sup>76,77</sup> and at high enough HNO<sub>3</sub> concentrations, reaction (28) rate is reduced, which is explained by U(IV) hydrolysis, favored as acidity decreases. The autocatalytic reaction occurs via the second hydrolysis product (U(OH)<sub>2</sub><sup>2+</sup>):<sup>73</sup>



Ermolaev and Krot<sup>78</sup> suggested that the oxidation of U(IV) in HNO<sub>3</sub> after the induction period follows a first order reaction equation, depending on the temperature and H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentrations. However, more complex decay equations are given by Koltunov<sup>75</sup> and Matsumoto.<sup>79</sup> Some authors have extrapolated the reaction rate constant of U(IV) with NO<sub>3</sub><sup>•</sup> radicals in aqueous solutions (24), based on the published reaction rates of other actinides with these radicals,<sup>80</sup> or have estimated this value from computer simulations,<sup>34</sup> or from the reaction of U(IV) with OH<sup>•</sup> radicals ( $8.6 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>) and U(IV) with SO<sub>4</sub><sup>-</sup> ( $1.2 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>) in acidic solutions.<sup>71</sup> The U(IV) reaction rate with NO<sub>2</sub><sup>•</sup> radicals was estimated by comparison with that for UO<sub>2</sub><sup>+</sup> + NO<sub>2</sub><sup>•</sup>.

The purpose of the present work is to examine the radiation chemistry of uranium (IV) in nitric acid solution in presence of HN and HAN. Pulse radiolysis investigations allow us to determine the reaction rates of NO<sub>3</sub><sup>•</sup> with U(IV), HN and HAN in HNO<sub>3</sub>/LiNO<sub>3</sub> solutions at room temperature (22.5°C), as well as at elevated temperature (45°C), similar to the temperature under PUREX operating conditions. This is the first time these reactions have been looked into directly, as it involves safe handling of actinides in a low oxidation state. Working with actinides presents scientific challenges in itself, but especially when combined with state of the art experimental methods like pulse radiolysis. The methodology developed involved an incremental approach:

initially, determination of kinetic rates for anti-nitrous agents and once the solutions' stability conditions defined, experimental measurement of kinetic rate for uranium (IV).

## Experimental

Nitric acid (69 wt.%) and lithium nitrate ultrapure grade (99.999%) were purchased from Sigma-Aldrich and VWR respectively, and used without further purification. Deionised water (18 M $\Omega$  cm and less than 10 ppb organic carbon) was used in all experiments. U(IV) stock solutions were prepared by catalytic hydrogenation of U(VI) nitrate in the presence of platinum. In order to prevent U(IV) hydrolysis and oxidation, nitric acid, hydrazinium or hydroxyl ammonium nitrate were added, yielding the following composition: U(IV) ~0.5 M, HNO<sub>3</sub> 1 M, HN 0.1 M or HAN 0.2 M. U(IV) samples were prepared by dilution of an aliquot of the stock solution in the corresponding electrolyte containing HN or HAN. For pulse radiolysis measurements, the total NO<sub>3</sub><sup>-</sup> concentration was set at 7 M, the solutions being formed by a mixture of LiNO<sub>3</sub> (6 M) and HNO<sub>3</sub> (1 M). An increase of the temperature from 25°C to 45°C leads to a reduction of the concentration of the species of 2% in molarity scale, due to the decrease of the density.<sup>81</sup> We took into account this variation in the spectrophotometric measurements for the calculations including the molar extinction coefficients. The stability of U(IV) solutions in these media at room temperature and 45°C was investigated by UV-Vis spectrophotometry (Shimadzu UV2501PC).

The decay of nitrate radicals in the presence of uranium (IV) with anti-nitrous agents was monitored using the pulse radiolysis system of ELYSE accelerator (Paris-Saclay University) that allows the generation and investigation of transient species with high time resolution, on time scales ranging from ps to ms. Laser (260 nm) driven Cs<sub>2</sub>Te photocathode allows the production of short electron pulses with a typical half width of 7 ps, charge of ~ 6 nC, and energy of ~7.8 MeV, at a repetition rate of 5 Hz.<sup>82</sup> The experimental line used for these investigations employs a highly dynamic Hamamatsu C7700-01 streak camera, coupled to a Chromex 250 IS spectrograph for detection, while the analyzing light is delivered by a home built xenon flash lamp.<sup>83</sup> Optical quartz cells with a path length of 1 cm for room temperature experiments, and 0.5 cm for high temperature experiments, were placed as close as possible to the output window of the accelerator to minimize the divergence of the electron beam. All measurements were obtained as an average of 750 acquisitions per scan. The sample was continuously flown using a peristaltic pump (flow rate ca. 20 cm<sup>3</sup>/min) for the high temperature experiments, in order to avoid degradation of the sample or accumulation of degradation products, and purged with argon gas continuously during the measurements. UV-Visible measurements were performed in the 400 to 700 nm wavelength range. The exploration of this wavelength domain made it possible to simultaneously follow the time evolution of nitrate radicals' spectrum intensity, and to verify that uranium in

our solutions is indeed in +IV oxidation state (Sup. Data-1). Quantification of the decay of the nitrate radical was carried out at 640 nm.

In order to reach the desired working temperature, we used a modified coil type condenser, placed before the entrance of the sample cell, equipped with an external heating cable, connected to a PID controller that allows the remote regulation of the temperature (with a precision of  $\pm 0.5^\circ\text{C}$ ). The temperature was measured on the external surface of the quartz cell and inside the heating coil with Pt-100 temperature sensors. The measurements were performed at  $22.5^\circ\text{C}$  and  $45^\circ\text{C}$ . Details about the heating system are presented elsewhere.<sup>56</sup> Special materials that are both acid and temperature resistant were used for these investigations in order to insure safe operation. (e.g., MasterFlex Chem-Durance Bio tubing).

The dose deposited per pulse was determined from measurements of the absorbance of solvated electrons ( $A_{e_{aq}}(\lambda, t)$ ) in water at  $22.5^\circ\text{C}$  and verified before each series of experiments, considering the initial yield of the solvated electrons, measured at 10 ps, to be  $G(10 \text{ ps}) = 4.5 \times 10^{-7} \text{ mol/J}$ ,<sup>84</sup> and its molar extinction coefficient  $\varepsilon_{715\text{nm}} = 19700 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>85</sup> The absorbance ( $A(\lambda, t)$ ) measured for a given species in highly concentrated solutions depends on the dose (D), extinction coefficient ( $\varepsilon_\lambda$ ) and the yield (G(t)) according to:

$$A(\lambda, t) = \varepsilon_\lambda \cdot l \cdot c(t) = \varepsilon_\lambda \cdot l \cdot D \cdot \rho \cdot G(t) \quad (\text{Eq. 1})$$

where  $l$  is the optical path-length,  $c(t)$  is the concentration of the investigated species at time  $t$ ,  $\rho$  is the density of the solution. All results presented herein were measured at an absorbed dose in water of 50 Gy per pulse.

## Methodology

The thermal instability and radio-sensitivity of  $\text{HNO}_3$ , leads to accumulation of  $\text{HNO}_2$  in solution and  $\text{NO}_2$  and NO ( $\text{NO}_x$ ) in gas phase, that affects the redox potential of the aqueous media. In order to prevent U(IV) oxidation in  $\text{HNO}_3$  media hydrazinium nitrate and hydroxyl ammonium nitrate were used to stabilize uranium in the +IV oxidation state. Moreover, in order to prevent U(IV) hydrolysis, the  $\text{HNO}_3$  concentration was fixed at 1 M. Simultaneously, to avoid a slow oxidation by oxygen, the atmosphere was controlled by bubbling Ar during all experiments.

The methodology developed for this study relies on the optimum choice of U(IV) and anti-nitrous agent concentrations in order to obtain a perfect stability of the U(IV) solution, especially at higher temperatures ( $45^\circ\text{C}$ ), and to ensure that nitrate radicals react with U(IV) and not with the anti-nitrous agent. Indeed, it has been confirmed during this work that these anti-nitrous agents react rapidly with the nitrate radical and these reactions will therefore be in competition with the oxidation of U(IV). Only scarce literature data exist on the stability of the U(IV) solutions (not relevant for our experimental conditions). It was therefore necessary, prior to the pulse radiolysis measurements, to establish the ratio between U(IV) to anti-nitrous agents concentrations that should be used. Spectrophotometric studies of U(IV) stability were performed for various ratios of [U(IV)] to anti-nitrous agents concentration. Preliminary work has

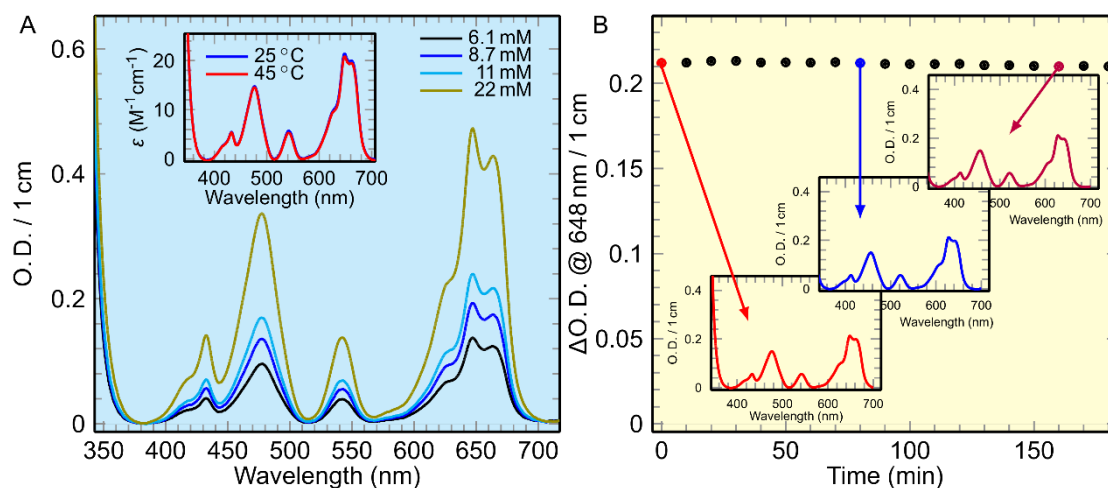


shown that it is necessary to use a mixture of both anti-nitrous agents hydroxyl ammonium and hydrazinium to obtain a solution of U(IV) stable at 45°C for at least 3 hours in HNO<sub>3</sub> medium (1 M) and LiNO<sub>3</sub> (6 M).

## Results

### Speciation of U(IV) in nitric acid media

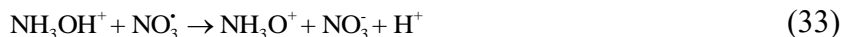
The speciation of U(IV) chemical form was investigated by UV-Visible spectrophotometry. Figure 1A shows the absorption spectra of the solutions used in this work. These spectra exhibit the characteristic absorption band of U(IV) centered at 647 nm.<sup>86-92</sup> A prior calibration of U(IV) in (H, Li)NO<sub>3</sub> 7 M in the presence of HN and HAN was performed at 25°C, over the U(IV) concentration range  $2.5 \times 10^{-3} - 5 \times 10^{-2}$  M, yielding a  $\epsilon_{647\text{nm}} = 21.4 \pm 0.1 \text{ M}^{-1} \text{ cm}^{-1}$ . The spectrophotometric absorption measurements of the uranium (IV) solution at 25°C and 45°C are presented in Figure 1. These measurements show that the molar extinction coefficient and the absorption maximum values do not depend on the temperature. Comparison of our results with those of Ikeda-Ohno et al. (performed by spectrophotometry and EXAFS)<sup>36</sup> clearly shows that in (H, Li)NO<sub>3</sub> 7 M medium, the uranium(IV) is complexed with 4 or 5 bidentate nitrate ions and that the coordination sphere is completed by 1 ([U(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)] or 2 water molecules ([U(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]). The presence of water molecules in the first coordination sphere of U(IV) is confirmed by the differences in the absorption spectra with those of the hexanitrate complex of U(IV) (U(NO<sub>3</sub>)<sub>6</sub>)<sup>2-</sup>.<sup>93</sup> The U(IV) solution is stable at least for a few hours during our experiments (Figure 1 Right). Performing the pulse radiolysis experiments, we verified the stability of the solutions by observing the absorption spectra of the solutions before and after the pulse.



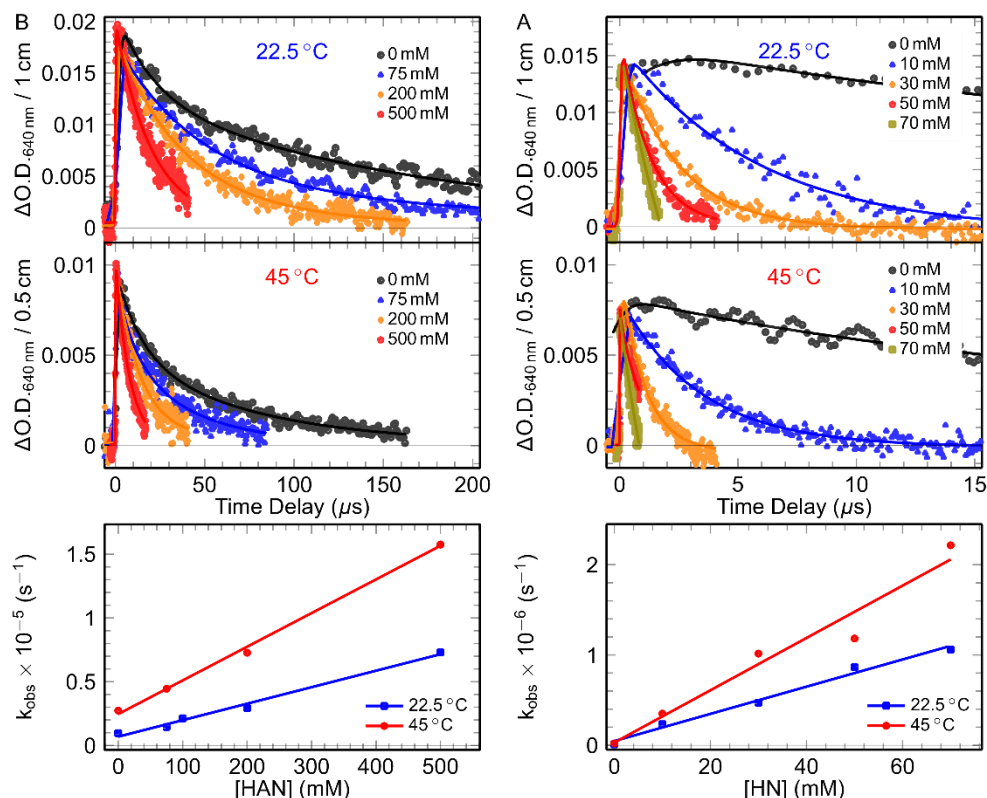
**Figure 1.** (Left) Absorption spectra of U(IV) at different concentrations at 25°C (LiNO<sub>3</sub> 6 M, HNO<sub>3</sub> 1 M, HAN  $7.7 \times 10^{-3}$  M, HN  $2.2 \times 10^{-4}$  M); Inset :Absorption spectra of U(IV)  $10^{-2}$  M at 25°C and 45°C (LiNO<sub>3</sub> 6 M, HNO<sub>3</sub> 1 M, HAN  $7.7 \times 10^{-3}$  M, HN  $2.2 \times 10^{-4}$  M). (Right) Stability of the solutions over time.

### Reaction between NO<sub>3</sub> radicals and HAN

In our experimental conditions, HAN exists under its protonated form  $\text{NH}_3\text{OH}^+$  and in order to understand the  $\text{NO}_3^\cdot$  radical reaction with HAN, we followed the time evolution of the absorption band of  $\text{NO}_3^\cdot$  radical at 640 nm for solutions of different concentrations of HAN (Figure 2). The kinetics at 640 nm show a faster decay with increasing concentration, indicating the occurrence of the investigated reaction. *Ab initio* calculations showed that the radical – hydroxylamine reaction can occur either via the cleavage of O-H (32) bond and formation of O-N bond (33),<sup>94</sup> or via H atom abstractions, as suggested by Pembridge et al:<sup>95,94</sup>



The decay of the nitrate radicals is extremely complex,<sup>59</sup> but in a first approximation, we consider the decay as a pseudo-first order and fit the recorded kinetics using a single exponential function. When adding HAN to the solution, we observe a faster decay, with a first order kinetics. The concentration of HAN is too low to be ionized directly and the main reactions of the radicals issued from radiolysis occur with  $\text{HNO}_3$ ,  $\text{H}^+$  and  $\text{NO}_3^-$ . By plotting the observed reaction rates as a function of the HAN concentration (Figure 2 right) we can determine the reaction rate. Based on our measurements, the reaction rate is  $1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  at 22.5 °C. As expected, at 45°C, an acceleration of this decay is observed, yielding a reaction rate of  $2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .



**Figure 2.** Time evolution of the absorbance at 640 nm, measured at 22.5°C (top image) and 45°C (middle image) in solutions containing different concentrations of hydroxyl ammonium (left) and hydrazinium (right), along with their pseudo-first order fit (Except for the decay at 22.5°C and 45°C in

the absence of HN. In these cases the solid line are drawn to guide the eyes). Observed reaction rates (bottom image) as a function of the concentration of HAN at 22.5°C (black) and 45°C (red).

### Reaction between $\text{NO}_3^\cdot$ radicals and $\text{N}_2\text{H}_5^+$

Previous studies gave contradictory values for the reaction rate between hydrazine ( $\text{N}_2\text{H}_4$ ) and nitrate radicals:  $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;<sup>96</sup>  $6.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>97</sup> A previous pulse radiolysis investigation in our group of hydrazine reactivity towards  $\text{NO}_3^\cdot$  radicals on in 7 M  $\text{LiNO}_3$ , 7 M  $\text{LiNO}_3 + 1 \times 10^{-3} \text{ M HNO}_3$  and 6.9 M  $\text{LiNO}_3 + 0.1 \text{ M HNO}_3$  allowed the extrapolation of the reaction rates between the two protonated forms of  $\text{N}_2\text{H}_4$  ( $\text{N}_2\text{H}_5^+$  and  $\text{N}_2\text{H}_6^{2+}$ ) and  $\text{NO}_3^\cdot$  radicals:  $k_{\text{N}_2\text{H}_5^+} = 2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{N}_2\text{H}_6^{2+}} = 1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at room temperature.<sup>59</sup>

The present conditions 1 M  $\text{HNO}_3 + 6 \text{ M LiNO}_3$  allow us to select only the  $\text{N}_2\text{H}_5^+$  protonated form of hydrazine in our system, and investigate the reaction:



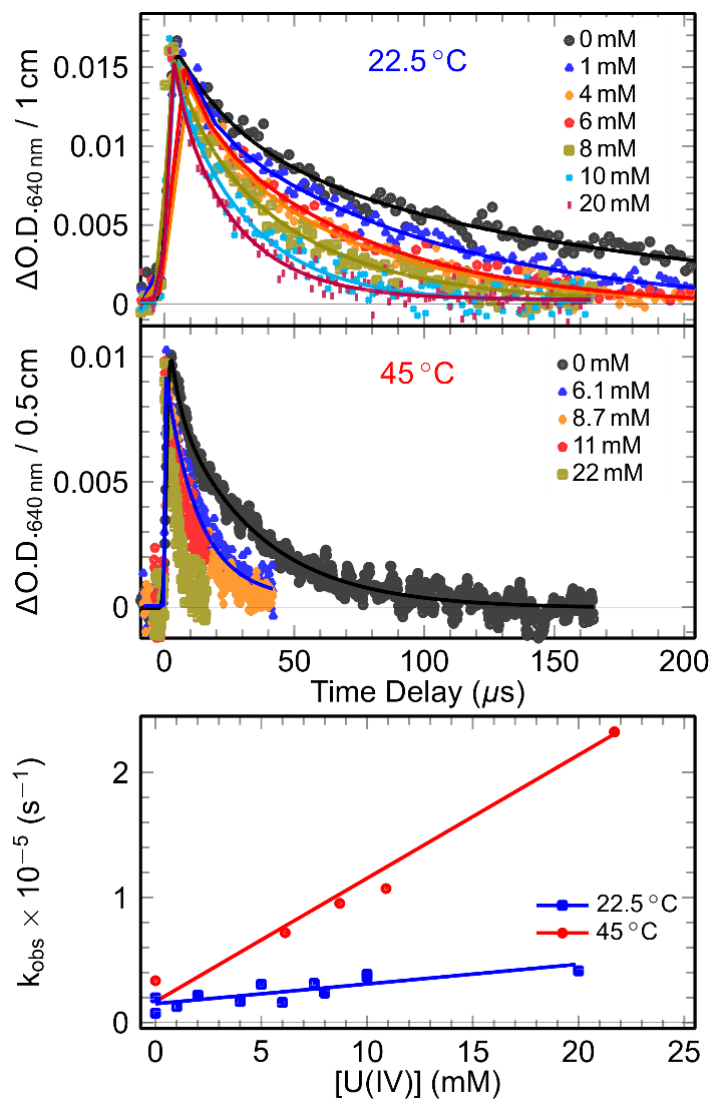
Figure 2 left presents the change in the  $\text{NO}_3^\cdot$  absorbance at 640 nm for 1 M  $\text{HNO}_3 + 6 \text{ M LiNO}_3$  in the absence and presence of hydrazine. As expected,  $\text{N}_2\text{H}_5^+$  concentration and temperature increase lead to a faster decay of the nitrate radical. From exponential fits of this decay, assuming the decay to be a pseudo-first order decay in the presence of hydrazinium, we can extrapolate the reaction rate constant for this reaction. At room temperature, the reaction rate is  $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , while the temperature increase leads to an acceleration up to  $2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . The values we determined are different from the ones previously reported by our group at room temperature ( $2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) and the differences can arise from the fact that the previous evaluations are based on calculations assuming an arbitrary value of 12.9 for the acid dissociation constant. At the same time, uncertainties over the  $\text{pK}_{a2}$  value (-1) for hydrazine exists, which may have induced errors on the previously reported values. It is interesting to note that the rate constant of the  $\text{NO}_3^\cdot$  decay is two orders of magnitude faster with hydrazinium (HN) than with HAN, showing a more powerful scavenging efficiency of hydrazinium.

### Reaction between $\text{NO}_3^\cdot$ radicals and U(IV)

To bind nitrous acid and stabilize the solutions at 45°C, a mixture of 7.7 mM HAN and 0.22 mM HN was added to the solutions of U(IV) to study the reactivity of  $\text{NO}_3^\cdot$  radicals towards U(IV) in six solutions all containing 1 M  $\text{HNO}_3 + 6 \text{ M LiNO}_3$  and with concentrations of U(IV) between  $1 \times 10^{-3}$  and  $2 \times 10^{-2} \text{ M}$  at the two temperatures.

Following the absorbance decay of nitrate radicals at 640 nm, we observe its faster decay when increasing the U(IV) concentration, indicating the oxidation of U(IV) by nitrate radicals. Using the methodology describe above, we determined the reaction rate constant for this oxidation reaction to be  $1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , and  $9.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at 22.5°C and 45°C, respectively. Note that this value found by direct observation at room temperature is

10 times smaller than previous reported values obtained by numerical simulations of the steady-state radiolytic yields measurements at room temperature ( $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>71</sup>



**Figure 3.** Absorption at 640 nm of  $\text{NO}_3^\bullet$  radicals measured at 22.5°C (top image) and 45°C (middle image) as a function of time from radiolysis of deaerated 1 M  $\text{HNO}_3$  + 6 M  $\text{LiNO}_3$  + 7.7 mM HAN + 0.22 mM HN, with different concentrations of U(IV). Bottom image: observed reaction rates as a function of the concentration of U(IV) at 22.5°C (black) and 45°C (red).

## Discussion and Concluding remarks

The behavior of nitric acid solutions under radiation is of great importance in the reprocessing of spent nuclear fuel, and based on the evaluated reaction rates, theoretical models, that can better predict the radiolytic process during the PUREX process, can be developed. These models are critical for defining safe operating practices and controls and engineered safety features. Knowledge gained from radiolytic experiments of HNO<sub>3</sub> solution provides insight on the role of these parameters and their interdependencies in promoting the reactions between NO<sub>3</sub><sup>•</sup> radicals and the PUREX process main components. The detailed mechanism of nitrate radicals reaction with hydrazinium, hydroxyl ammonium and U(IV) has been elucidated through a pulse radiolysis investigation of HNO<sub>3</sub>/LiNO<sub>3</sub> 1/6 M solutions at 22.5°C and 45°C. We defined the conditions to stabilize U(IV) in nitrate solution against thermal oxidation while using the smallest possible amounts of HN and HAN that allows us to observe directly the reaction between U(IV) and NO<sub>3</sub><sup>•</sup> by pulse radiolysis at room temperature and at 45°C. The thus evaluated rate constants are summarized in Table 2.

**Table 2.** Reaction rate constants measured during this pulse radiolytic investigation of 1 M HNO<sub>3</sub> + 6 M LiNO<sub>3</sub> at 22.5 and 45 °C

Reaction	k ( M <sup>-1</sup> s <sup>-1</sup> )		Estimated activation energy (kJ/mol)
	22.5°C	45°C	
NH <sub>3</sub> OH <sup>+</sup> + NO <sub>3</sub> <sup>•</sup>	1.3 × 10 <sup>5</sup>	2.6 × 10 <sup>5</sup>	22
N <sub>2</sub> H <sub>5</sub> <sup>+</sup> + NO <sub>3</sub> <sup>•</sup>	1.5 × 10 <sup>7</sup>	2.9 × 10 <sup>7</sup>	21
U(IV) + NO <sub>3</sub> <sup>•</sup>	1.6 × 10 <sup>6</sup>	9.3 × 10 <sup>6</sup>	56.3

The radical NO<sub>3</sub><sup>•</sup> is known to oxidize by a one electron transfer reaction. The rate constants obtained for the electron transfer between NO<sub>3</sub><sup>•</sup> and the three scavengers are all lower than the diffusion limit by several orders of magnitudes, showing the presence of an activation barrier.

At room temperature hydrazinium scavenges the NO<sub>3</sub><sup>•</sup> radical 100 times faster than hydroxyl ammonium. The reactivity of U(IV) towards NO<sub>3</sub><sup>•</sup> is 10 times slower than that with hydrazinium and 10 times faster than that with hydroxyl ammonium. For these reasons, it was important to define the optimum concentration ratios to be used in order to observe experimentally the reaction of NO<sub>3</sub><sup>•</sup> with U(IV).

The direct observation of radical NO<sub>3</sub><sup>•</sup> in the presence of U(IV), gives us a rate constant at least 10 times lower than the value currently used, which has been estimated by comparing the oxidation rate with other oxidizing radicals. It is clear that this difference with the reported estimated rate constant value cannot be explained by the difference of the ionic strength, because this latter does not strongly affect the kinetics when the solutions have high ionic strength where the Debye law is no longer valid. It is important to note that the oxidation rate constant depends strongly on the complexation state of the ions. For example, it is reported that the rate constant of the oxidation reaction of U(IV) by OH<sup>•</sup> radicals is 8.6 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>. However, it is not possible to

measure this rate constant in highly concentrated nitric solution because  $\text{OH}^\cdot$  is almost entirely scavenged by  $\text{HNO}_3$  and U(IV) is no longer in the +IV oxidation state in such solutions. However, it is interesting to compare the rate constant of oxidation by  $\text{NO}_3^\cdot$  with that by  $\text{NO}_2^\cdot$ : the reaction rate constant is  $10^4$  times larger with  $\text{NO}_3^\cdot$  than with  $\text{NO}_2^\cdot$ . Note that the oxidation potential of  $\text{NO}_2^\cdot/\text{NO}_2^-$  is around 1 V/NHE<sup>98</sup> and that of  $\text{NO}_3^\cdot/\text{NO}_3^-$  is close to 2.5 V/NHE.<sup>99</sup> It was reported that the oxidation rate of U(IV) by  $\text{SO}_4^\cdot$  in sulfuric acid is  $7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>71</sup> When comparing our results, we can conclude that U(IV) is complexed by nitrate ions which is different than complexation by in sulfuric acid, changing the redox potential.

Although reprocessing of spent nuclear fuel occurs at moderate temperatures (close to 45°C for separation steps), up to now, no data on the rate constants of U(IV) oxidation have been reported, due to the complex conditions for direct measurements. The reaction rate constant values are influenced by the temperature and these modification can impact the ratio of the competitive reactions. Therefore, it is important to measure the rate constants at temperatures simulating the separation process conditions. We found that at 45°C, the rate constant of the reaction with hydroxyl ammonium and hydrazinium, is increased by almost a factor of 2. The estimated activation energy should be larger for U(IV), because the rate constant becomes 6 times faster at 45°C compared to 22.5 °C (Table 2).

The results reported show the complexity of the solutions usually used in the spent nuclear fuel reprocessing. The reported data are key input information for the simulations codes dedicated to the radical chemistry of reprocessing process in nuclear industry. The similar approaches should be adapted to study the role of Pu and associated rate constants.

## Conflicts of interest

There is no conflict to declare.

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