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Redox Reactions of Pu ions in Aqueous Nitric Solutions under Ultrasound Irradiation

Virot M.,¹ Venault L.,² Moisy P.,² Nikitenko S. I.¹

¹ ICSM-UMR5257 CNRS/CEA/UM2/ENCSM, Site de Marcoule, 30207 Bagnols/Cèze, France ; ² CEA/DEN/DRCP, Radiochemistry and Process Department, 30207 Bagnols/Cèze, France. Email: matthieu.virot@cea.fr

INTRODUCTION

In France, industrial reprocessing of spent nuclear fuel involves the dissolution of the irradiated fuel in concentrated nitric media in view of the recycling and separation of uranium and plutonium. Among others, the current treatment of spent fuel raises the questions of waste and effluent management. With the aim of preparing future GENIV reactors and answering to the world demand in the development of a more sustainable nuclear energy, new alternatives are nowadays investigated [1,2]. Sonochemistry, which studies the influence of ultrasonic waves on chemical systems, has been showed to enhance chemical yields and accelerate reaction rates for several homogeneous and heterogeneous systems [2,3]. The aim of the present study is to evaluate the potential of high-power ultrasound towards the control and stabilization of Pu oxidation states in aqueous nitric solution.

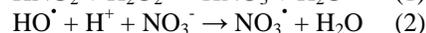
DESCRIPTION OF THE ACTUAL WORK

Aqueous nitric solutions of Pu(III), Pu(IV), and Pu(VI) were submitted to 20 kHz ultrasound irradiation (0.28 – 0.52 W mL⁻¹) under Ar atmosphere. Experiments were carried out in Atalante facility (Marcoule) in a dedicated glove box allowing the control of the temperature in the home-made reactor during the whole experiments (25-29°C). The acoustic power delivered to the solution was assessed by using the calorimetric method. The behavior of the sonicated Pu solutions was studied in 1 M HNO₃ and was followed by using the UV-Vis-NIR spectrophotometer connected to the glove box. Pu(VI), Pu(V), Pu(IV) and Pu(III) were respectively followed at 831 nm ($\epsilon = 530 \text{ cm}^{-1} \text{ M}^{-1}$), 568 nm ($\epsilon = 19 \text{ cm}^{-1} \text{ M}^{-1}$), 476 nm ($\epsilon = 67 \text{ cm}^{-1} \text{ M}^{-1}$), and 602 nm ($\epsilon = 30 \text{ cm}^{-1} \text{ M}^{-1}$). The formation rate of H₂O₂ during sonolysis was determined by colorimetric method: sampled solution aliquots were diluted with a 2.10⁻² TiOSO₄ solution, and the formation of a [Ti(IV)H₂O₂] complex was followed at 410 nm ($\epsilon = 730 \text{ cm}^{-1} \text{ M}^{-1}$).

RESULTS

The sonication of pure water under Ar is known to generate H₂ and H₂O₂ species resulting from the recombination of radical products formed by the homolytic dissociation of H₂O molecules [2]. Previous investigations demonstrated that the sonication of aqueous

nitric solutions leads to the formation of NO and NO₂ in the gas flow, and the accumulation of HNO₂ in solution [3,4]. Using these conditions, H₂O₂ cannot accumulate due to its rapid reaction with HNO₂ according to the reaction 1. In the presence of anti-nitrous reagents, the accumulation of H₂O₂ becomes possible and is even higher than what usually observed in pure water for similar conditions. This phenomenon results from the reaction of OH[•] radicals with nitrate ions, followed by their hydrolysis (reactions 2-3) [5]. In this mechanism, only one HO[•] radical is used to produce one H₂O₂ molecule, while two HO[•] are needed in pure water.



The sonolysis of various Pu solutions was studied in diluted aqueous nitric solutions (20 kHz, Ar, 1 M HNO₃). The ultrasonic treatment of such a solution has no effect on Pu(IV). By contrast, Pu(III) is found to be rapidly oxidized to Pu(IV) in similar conditions. The reaction mechanism involves the catalytic oxidation of Pu(III) with nitrous acid generated by nitric acid sonolysis. In the presence of sulfamic acid or hydrazinium nitrate as anti-nitrous reagents (reactions 4-5), Pu(IV) is found to be reduced to Pu(III) during ultrasound irradiation (Fig 1). The reaction kinetics follows a first order reaction law and is highly dependent upon the acoustic power delivered to the solution.

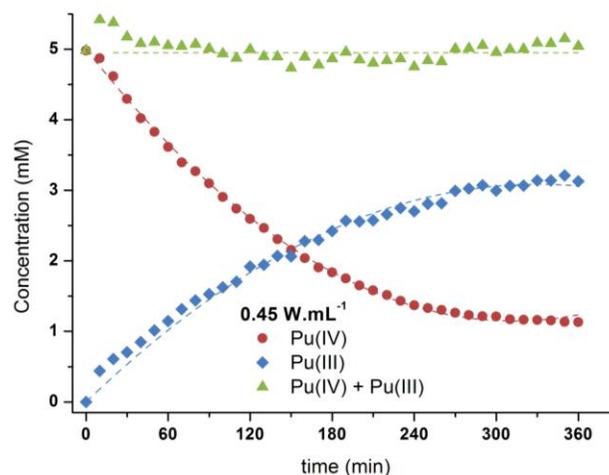
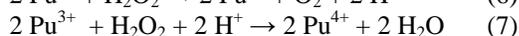
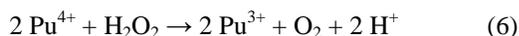
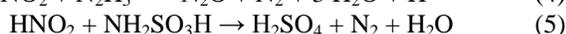


Fig. 1. Sonolysis (20 kHz, 0.45 W mL⁻¹, Ar, V= 50 mL) of a 5 mM Pu(IV) solution in 1 M HNO₃ / 0.1 M NH₂SO₃H.

Pu(IV) reduction is not complete and leads to a steady state where Pu(IV) and Pu(III) are both coexisting in solution. In the presence of Pu ions, the absence of H₂O₂ in sonicated solutions was evidenced by UV-Vis spectroscopy. In agreement with the literature, the decrease of Pu(IV) concentration during sonolysis can be attributed to its reduction reaction with the in-situ generated H₂O₂ (reaction 6) [6]. Investigations showed that the steady state is explained by the partial back oxidation of Pu(III) with H₂O₂ in agreement with the reaction (7).



The concentration of Pu(VI) in diluted aqueous nitric solution in the presence of sulfamic acid is also found to decrease during sonication. The reduction reaction leads to Pu(V) accumulation (Fig. 2) and can be attributed to the in-situ formation of H₂O₂ [6]. Note that Pu(V) is normally unstable in these conditions but is found to accumulate as a result of the continuous Pu(VI) reduction by ultrasound. For prolonged sonication, the presence of Pu(IV) resulting from Pu(V) disproportionation is evidenced. Furthermore, the kinetics related to Pu(VI) reduction are found to increase with sonication time. This phenomenon could be explained by the reduction of Pu(IV) to Pu(III) with H₂O₂ in agreement with the above described results. Pu(III) could then react with Pu(VI) according to the well-known equilibrium described in the reaction (8), and therefore explain the acceleration of Pu(VI) reduction rate during sonication.

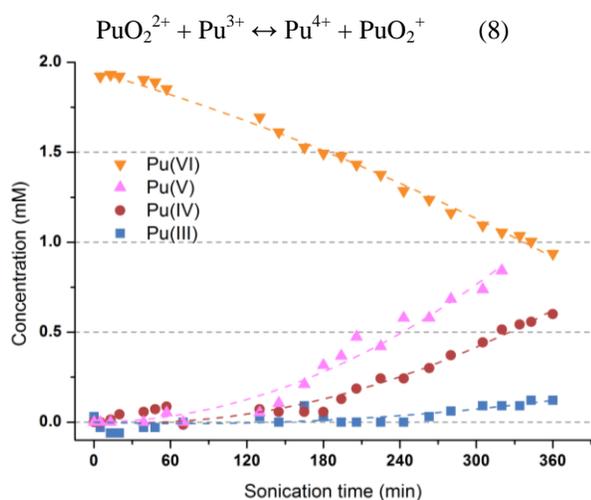


Fig. 2. Sonolysis (20 kHz, 0.48 W mL⁻¹, Ar, V= 50 mL) of a Pu(VI) solution in 1 M HNO₃ / 0.1 M NH₂SO₃H. Pu(V) and Pu(IV) concentrations are increasing with sonication duration (Pu(III) signal has to be confirmed).

Sonochemistry appears to be an interesting and valuable tool for the control and stabilization of actinide species in solution. The procedure allows working under controlled kinetics by generating active species directly in the solution without any additional chemicals. Sonication is in addition performed in dilute nitric solutions at almost room temperature what can be of particular interest in nuclear processing. Further experiments are currently under investigation to enhance kinetics.

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