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Effect of Gamma Irradiation on the Oxidation State of Neptunium in Nitric Acid in the Presence of Selected Scavengers

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A series of experiments was performed with selected reagents that were added to inhibit the reduction of Np(VI) to Np(V) during irradiation of its solutions in HNO_3. Acetamide and methylurea as nitrous acid scavengers, and vanadium(V) as a neptunium(V) oxidizer, were examined in this effort. Solutions of these reagents in 4 M HNO_3 were irradiated in a Co-60 gamma irradiator. Additions of 1-10 mM of methylurea and vanadium(V) essentially had no effect on the final oxidation state of Np after irradiation with a dose of 60 kGy, while the addition of higher concentrations of methylurea (50 and 100 mM) led to an almost complete reduction of Np to the tetravalent oxidation state.

Keywords acetamide; irradiation; methylurea; neptunium; nitrous acid

INTRODUCTION

During the reprocessing of used nuclear fuel (UNF) solutions, Np(VI) is reduced to Np(V) by radiolytic degradation products. In particular, nitrous acid (HNO_2), which is produced by the radiolysis of nitric acid, causes significant reduction of Np(VI). Formation of Np(V) is undesirable, as it is poorly extracted by TBP. A series of experiments was performed in an attempt to inhibit this reduction. Vanadium(V) was used to reoxidize Np(V) back to Np(VI). Methylurea (MU) and acetamide (AcA) were used to prevent the formation of HNO_2.

Radiolysis of Nitric Acid

Radiolysis of aqueous solutions of nitric acid mainly produces gaseous compounds such as H_2, O_2, and N_2 while producing significant amounts of HNO_2 and H_2O_2. The latter two are mutually reactive:

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \qquad (1)$$

Hydrogen peroxide is not present in solutions after irradiation if the radiolytic production of HNO_2 was significantly higher. This happens in solutions with HNO_3 concentration greater than 0.5 M ($= 0.5\,\mathrm{mol/dm^3}$). Production of HNO_2 is proportional to the concentration of nitrate anion; however, its radiation yield decreases with the acidity of the aqueous solution: the production of HNO_2 in solution of 0.1 M HNO_3 + 5.9 M $NaNO_3$ was almost 3 times higher than in 6 M HNO_3 (1). Low linear energy transfer (LET) radiation like β and γ has radiation yields around 0.25 mM/kGy in 1 M HNO_3. The radiation yields by α particles are approximately two times lower (2).

Importance of HNO_2

The significance of HNO_2 in the redox speciation of neptunium is based on its reducing behavior toward Np(VI). The reduction of Np(VI) to Np(V) is not complete, as the reaction extent is controlled by an acidity-dependent equilibrium (3,4) in which the nitrous acid acts as a catalyzer of oxidation of Np(V) by the effect of nitrate:

$$NpO_2^+ + \frac{3}{2}H^+ + \frac{1}{2}NO_3^- \xrightleftharpoons{catal.HNO_2} NpO_2^{2+} + \frac{1}{2}HNO_2 + \frac{1}{2}H_2O \qquad (2)$$

The traditional approach to eliminate HNO_2 from HNO_3 solutions uses sulfamic acid or ferrous sulfamate $Fe(NH_2SO_3)_2$, where the sulfamate anion reacts with HNO_2 and produces nitrogen gas and sulfate anion, which is another undesirable compound in the separation streams (5). Therefore, the general effort towards reducing of the amount of radioactive waste from the reprocessing of

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UNF necessitates the use of "salt-free" compounds that consist only of C, H, N, and O elements, and as fully combustible, they will not add to the weight and volume of the high level wastes from UNF reprocessing.

Methylurea and Acetamide

Recently, primary and secondary amides such as acetamide (AcA) and methylurea (MU), respectively, were proposed as possible scavengers for nitrous acid (Fig. 1). It is well known that these compounds are reactive towards HNO_2 (6,7). Methylurea reacts with HNO_2 through a nitrosation reaction (Fig. 2) (7). This forms N-nitrosomethylurea (NMU) by an attack of the NO^+ intermediate (produced by the protonation of HNO_2) on the carbonyl oxygen, which is followed by deprotonation and rearrangement of the NO group (8). Since NMU is not reactive towards Np(VI), methylurea functions as an efficient inhibitor of Np(VI) reduction by HNO_2.

The reaction of acetamide with HNO_2 is similar to the reaction of other primary amides, such as urea, which results in the production of gaseous nitrogen (9). The rate of the reaction (3) that leads to the elimination of HNO_2 is considerably slower than in the case of methylurea(6).

$$CH_3CONH_2 + HNO_2 \rightarrow CH_3COOH + N_2 + H_2O \quad (3)$$

Redox Reactions of Np with HNO_2 and Vanadium(V)

Pentavalent vanadium V(V) is a fast oxidizing agent towards Np(V), as 90% of the reaction is complete within several minutes for mM concentrations of V and Np. V(V) can be used as a holding oxidant in an attempt to keep neptunium in its hexavalent oxidation state, as described by the following reaction:

$$NpO_2^+ + VO_2^+ + 2H^+ \leftrightarrows NpO_2^{2+} + VO^{2+} + H_2O \quad (4)$$

The concentration equilibrium constant for this reaction in 4 M perchloric acid/perchlorate system was determined to be $0.13 \pm 0.02\,M^{-2}$ (10). Raising the nitric acid concentration from 1 to 4 M leads to a significant shift of the reaction (4) from left to right with the equilibrium ratio of [Np(VI)]/[Np(V)] increasing 16 times for a given ratio of [V(IV)]/[V(V)].

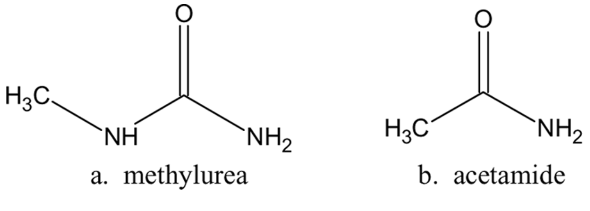
a. methylurea b. acetamide

FIG. 1. Proposed nitrous acid scavengers.

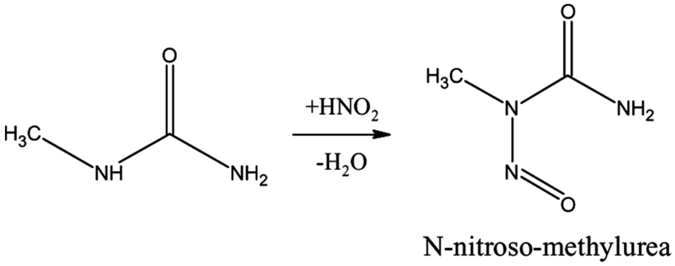

FIG. 2. Methylurea nitrosation.

EXPERIMENTAL

UNF from light water reactors cooled for 150 days have a 20 kW/t heat production (5), which assumes that a 1 M concentration of uranium after the fuel dissolution will have an estimated dose rate well below 100 kGy/hr; hence, integral doses of up to 61 kGy were applied. Aerated solutions with additions of MU, AcA, V(V), and Np in HNO_3 were irradiated in hermetically enclosed glass vials or screw-cap polypropylene extraction vials in a gamma irradiator (^{60}Co) with a dose rate of 445 Gy/hr. Due to a small dose rate available, relatively long exposure times were needed; hence, the irradiation was not repeated. A relatively small dose rate did not significantly increase the temperature of the irradiated solutions above the ambient laboratory temperature. For correct evaluation of the radiation changes, the reference samples (the non-irradiated portions of studied solutions) were stored at the ambient temperature (22°C) during the same time as the irradiation time, and were analyzed together with the irradiated solutions.

All spectrophotometric analyzes were replicate. The differences in speciation results were within ±5% uncertainty for each species fraction.

Neptunium

^{237}Np ($t_{1/2} = 2.1 \times 10^6$ y) was received as NpO_2 from Argonne National Laboratory and dissolved in a slight molar excess of H_2O_2 and 8 M HNO_3. Confirmation of the tetravalent oxidation state was determined using Vis-NIR spectroscopy. In order to remove any transuranic impurities, the Np solution was added to a prepared BioRad AG-1 anion exchange column. The column was rinsed with a solution of 8 M HNO_3, 0.3 M hydrazine monohydrate, and 2 g/L hydroquinone. Np was stripped from the column using 0.36 M HCl and its isotopic purity was confirmed using thin-window HPGe gamma spectroscopy. Any organic impurities were destroyed by concentrated nitric acid and hydrogen peroxide. The clean solution of Np in 4 M HNO_3 had its oxidation state adjusted to hexavalent in a custom-made electrolytic H-cell by electrolysis on a Pt wire electrode at potential +1.3 V vs. reference Ag/AgCl electrode. The electrolysis was controlled by a BASi Epsilon™ e2 potentiostat.

UV-VIS-NIR spectroscopy of solutions in 1 cm path-length quartz cuvettes in spectral ranges of 200–1000 nm (OceanOptics^{TM} QE65000 spectrometer with DH-2000 BAL light source) and 900–1300 nm (Olis$^{®}$ RSM 1000 Monochromator, equipped with a 800 nm high-pass filter, InGaAs detectors and a tungsten halogen light source) was employed in order to determine the quantitative redox speciation of neptunium between Np(IV), Np(V), and Np(VI) by fitting to digitized published reference spectra (11).

Nitrous Acid

Preparation of HNO_2 for analysis of its absorption spectra was performed by mixing a spike consisting of a neutral solution of concentrated $NaNO_2$ in the nitric acid solutions. UV-VIS spectroscopy (RSM 1000 equipped with a Xe arc lamp or QE65000) was used for identification and quantification of HNO_2 and its interaction with methylurea and acetamide. The HNO_2 solutions have a distinctive absorption pattern between 350 and 400 nm. This pattern interferes somewhat with the broad and intensive absorption of HNO_3 in the shorter wavelength region. While $NaNO_2$ is stable in neutral solutions, the concentration of HNO_2 in strongly acidic solutions exposed to air significantly decreases over the course of 1–2 hours; therefore, the spectral analysis of both non-irradiated and irradiated solutions were performed within minutes after removal from the irradiator and opening the vial containing the solution.

Methylurea

Concentration of MU was quantified by spectrophotometric titration. Aliquots of irradiated or non-irradiated reference solutions were diluted 10- or 20-times in 1 M HNO_3 and then titrated by a 0.100 M aqueous solution of $NaNO_2$. Absorbance of the newly formed NMU was observed in a magnetic stirred 1 cm path-length quartz cuvette by the QE65000 spectrometer at 415 nm where it was the only absorbing species. Repeated titrations of methylurea aliquots led to an estimate of a ±5% uncertainty in the MU concentration value determined. Two sets of experiments were performed. It was presumed that the concentration of Np in dissolved UNF solutions is approximately 1 mM, so a range of 1–15 mM concentrations of reactants was chosen for the initial set of experiments. The second set of experiments was performed with 50–100 mM of methylurea.

RESULTS AND DISCUSSION

Nitrous Acid (HNO_2) Radiolytic Production

Solutions containing $1-8$ M HNO_3 concentrations were irradiated for several days and concentrations of HNO_2 were determined by absorption spectroscopy in the wavelength range of 350–390 nm. Production of HNO_2 increases with dose (Fig. 3) and with the initial concentration of HNO_3, and evidently, a significant amount (mM) of HNO_2 can be produced and affect the chemistry of Np in extraction systems. However, due to either the instability of HNO_2 in nitric acid or its interaction with radiolysis products, the rate of HNO_2 production at higher doses (>30 kGy) decreases.

Methylurea

Experiments with $NaNO_2$ solutions in HNO_3 have shown that MU very rapidly combines with HNO_2. MU itself has not been observed in the UV-VIS spectrum of its solution in HNO_3, but it can be identified due to the formation of NMU. The absorption spectrum of the NO group is altered, as its amplified absorption band is widened with the resulting broad maximum shifting to longer wavelengths (Fig. 4).

Additions of 1–10 mM MU in 4 M HNO_3 did not prevent the formation of significant quantities of HNO_2 during irradiation. Almost all MU/NMU was decomposed during the irradiation, as determined by the nearly unaltered spectra of HNO_2 that was produced during irradiation. Only the solutions with initial MU concentration 8 and 10 mM have slightly amplified spectra, indicating, that a small fraction of MU might have endured the effects of irradiation.

As a result of insufficient radiolytic stability of MU, experiments with larger concentrations of MU were also performed. Solutions of MU of varying concentration (5–500 mM) in 4 M HNO_3 were prepared. In addition to

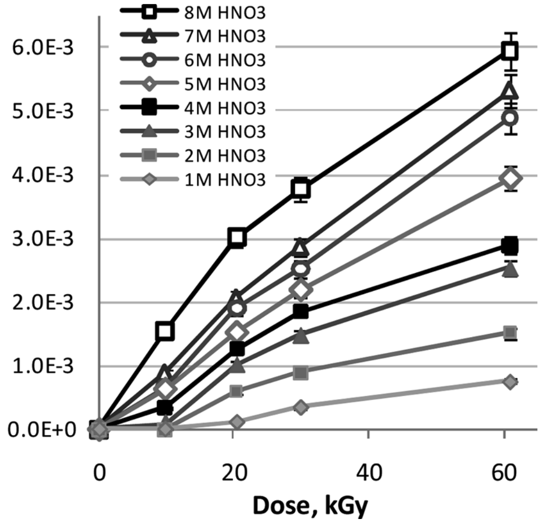

FIG. 3. Increase of the final concentration of HNO_2 produced by radiolysis of aqueous solutions of HNO_3 as a function of the effect of radiation dose (irradiation time). For the non-replicate measurements, a ±5% error associated with the spectrophotometric measurements is indicated.

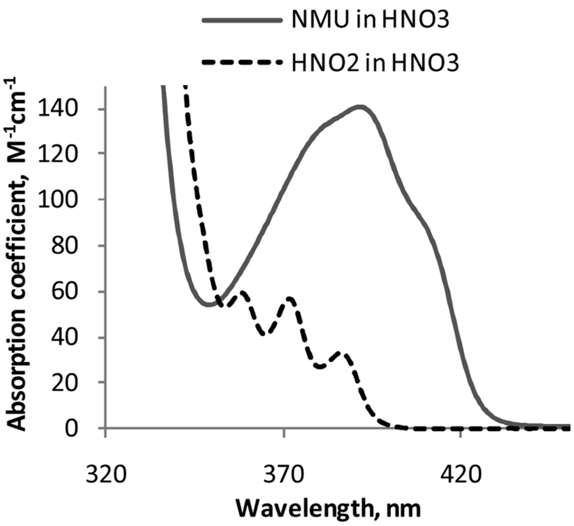

FIG. 4. Change of UV absorption spectrum of HNO_2 in HNO_3 by addition of methylurea (MU). The new characteristic spectrum can be easily distinguished from the spectrum of HNO_2 in HNO_3. The MU itself does not have any absorption spectrum in the UV-Vis region.

previous experiments with low concentrations of MU, 10 mM $NaNO_2$ was added to the mixtures to simulate the presence of HNO_2 at the moment of utilization of the scavenger in a real separation process.

In Fig. 5, the absorption spectra of post-irradiated solutions are compared. A decreasing trend in the final concentration of HNO_2 was observed for samples with MU concentrations of 5, 10, and 20 m M, with no free HNO_2 detected in samples with the MU concentrations of 100 and 500 m M. Concentration of HNO_2 bound with MU as nitroso-methylurea (Fig. 4) was smaller than expected; a small increase in the post-irradiation concentration of NMU was observed for the initial concentrations of MU from 100 to 500 mM for which there is so far no conclusive explanation. Only a very small part of the NMU formed by either the reaction of MU with the initial 10 mM HNO_2 or new HNO_2 formed by radiolysis of HNO_3 was observed. These results suggest that NMU is unstable in HNO_3 either by itself or degrades during irradiation.

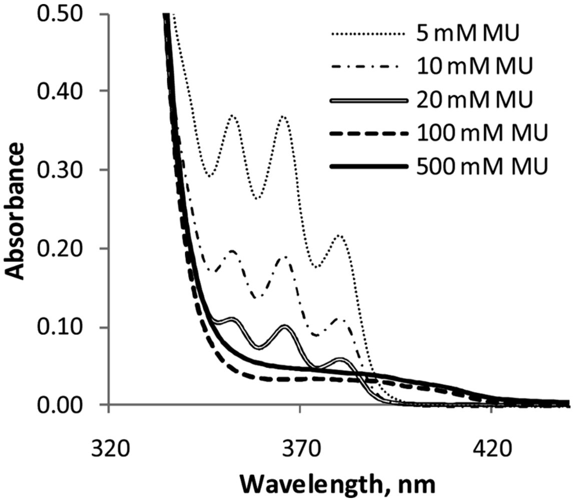

FIG. 5. Changes in absorbance spectrum of solutions of 4 M HNO_3 with initial additions of 10 mM $NaNO_2$ and variable concentrations of methylurea (MU) after irradiation by a dose of 40.5 kGy.

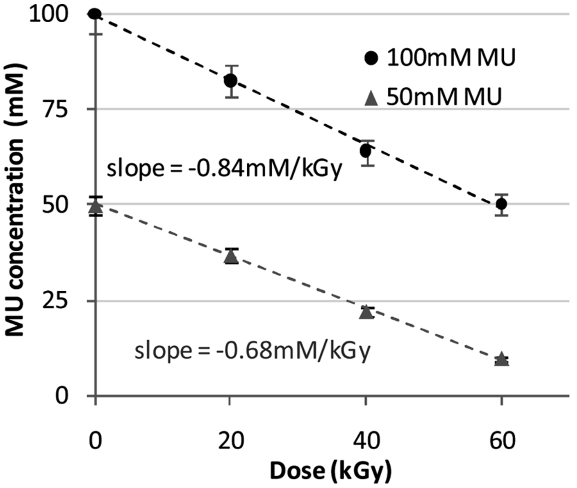

FIG. 6. Degradation of 50 and 100 mM solutions of MU in 4 M HNO_3 by radiolysis; Non-replicate measurements, error bars indicate a ±5% uncertainty range of the analytical method.

Methylurea Degradation by Gamma Irradiation

Solutions of 50 and 100 mM MU in 4 M HNO_3 were subjected to doses of 20, 40, and 60 kGy. Any remaining MU was determined by a spectrophotometric titration with $NaNO_2$. Titration of the non-irradiated reference solutions of MU at the dose-equivalent time intervals showed no degradation of MU caused by a concentrated nitric acid.

The concentration of methylurea decreases linearly with dose (Fig. 6). Only a small decrease in the radiolytic yields from 0.84 mM/kGy to 0.68 mM/kGy was observed for the solutions with 100 mM and 50 mM MU, respectively. This indicates that MU is being consumed by reactions with compounds or radicals that are produced by radiolysis at a constant rate.

Acetamide

The addition of AcA had very little immediate effect on the spectrum of HNO_2. This is in agreement with the findings of Plimmer (6), who has observed significant evolution of N_2 gas caused by reaction (3) only in the course of several hours. Therefore, only the post-irradiation effects are presented. The initial concentrations of 1–15 mM AcA caused none or only a very small decrease of the final concentration of radiolytically produced HNO_2. Because of the long irradiation time, the AcA should have already extensively reacted with HNO_2, and, therefore, has been either completely consumed by the produced HNO_2 or degraded by the radiolysis.

Effect of Addition of Vanadium(V)

The addition of vanadium(V) did not seem to have any effect on the final redox speciation of neptunium after irradiation, despite a 5-fold excess of V(V), indicating that the oxidizing ability of vanadium has decreased during the irradiation. It was experimentally confirmed that V(V) is not directly reduced to V(IV) by HNO_2; therefore, it is likely reduced either by intermediate products of radiolysis or indirectly by Np(V) generated from reduction of Np(VI) by HNO_2.

Effect of Low Concentrations of MU and V(V) on the Redox Speciation of Neptunium after Irradiation

Solutions containing about 2 mM Np(VI) in 4 M HNO_3 and various concentrations of MU and vanadium(V) were irradiated with a dose of 0–61 kGy. The initial ratio of Np(VI):Np(V) was 95:5. A synergistic effect of the scavenging properties of MU towards HNO_2 and oxidizing properties of V(V) towards Np(V) were expected. It was assumed that if any HNO_2 was produced, it would be scavenged by MU. Moreover, if any Np(V) was produced by HNO_2, it would be re-oxidized back to Np(VI) by V(V).

However, it was found that neither the presence of 1–10 mM MU or 1–10 mM V(V) nor the combination of 10 m M MU and 10 m M V(V) affected the reduction of Np(VI) to Np(V) with respect to the scenario of the absence of MU and addition of V(V). The ratio Np(VI):Np(V) decreased down to 50:50 in all cases.

The findings are a consequence of the fact that at a dose level of 61 kGy, all the 1–10 mM MU initially added has decomposed. More interestingly, the addition of vanadium(V) also did not alter the result, despite being in a 5-molar excess. Using higher concentrations (on the order of 50 mM) of V(V) as a holding oxidant is of course possible and has been exploited in the past (12), but the consequential substantial increase in the weight of non-evaporable residues in the high level waste is not likely to be desired in a real separation process.

Effect of High Concentrations of Methylurea on the Redox Speciation of Neptunium after Irradiation

As the experiments with concentrations of MU below 10 mM were unsuccessful in preventing the reduction of Np(VI), new sets of irradiations with larger additions of MU were performed. Solutions of 1.3 mM neptunium (initial redox speciation was 5% Np(V) and 95% Np(VI)) in 4 M HNO_3, containing 50 and 100 mM MU were subjected to integral doses of gamma radiation of 20, 40, and 60 kGy, and compared with their reference sample (a non-irradiated portion of the same solution, stored aside during the irradiation process). Analysis of the reference samples, presented in Fig. 7, showed that a very slow reduction of Np(VI) into Np(V) in 4 M HNO_3 occurs even without the influence of irradiation. After ~7 days, the initial ratio of Np(VI):Np(V) dropped from ~95:5 to ~75:25; however, the extent of Np(VI) reduction is clearly not significant enough to explain the changes taking place during irradiation (see below). This slow reaction is also not likely to be of importance in the shorter time-scales of real reprocessing conditions.

Redox speciation of irradiated samples was determined spectrophotometrically and is shown in Fig. 8. Surprisingly, the reduction of Np(VI) was actually enhanced by the presence of higher concentrations of MU and progressed during the radiation exposure, resulting with Np(IV) as the dominant redox state of neptunium. The reduction reaction was faster for the samples with initial concentration of 100 mM MU than with 50 mM MU; upon a dose of 40 kGy, the ratio of Np(IV):Np(V) reached approximately 10:1, and additional 20 kGy did not cause any significant change.

As stated in the introduction above, the presence of hydrogen peroxide is negligible in solutions with higher HNO_3 concentrations, because it reacts with HNO_2 by reaction (1). However, since the nitrous acid is removed from the system by addition of MU, the concentration of H_2O_2 may grow and significantly affect Np speciation even in 4 M HNO_3. As shown in Fig. 8, all Np(VI) is first reduced to Np(V), which can be explained by the reaction with H_2O_2 (13,14).

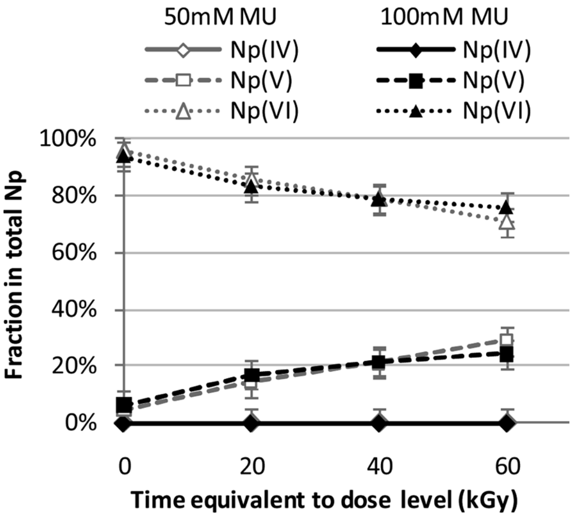

FIG. 7. Time dependent change of redox speciation of 1.3 mM Np in aq. 4 M HNO_3 containing 50 mM and 100 mM methylurea of non-irradiated reference solutions. For the non-replicate measurements, a ±5% error associated with the spectrophotometric measurements is indicated.

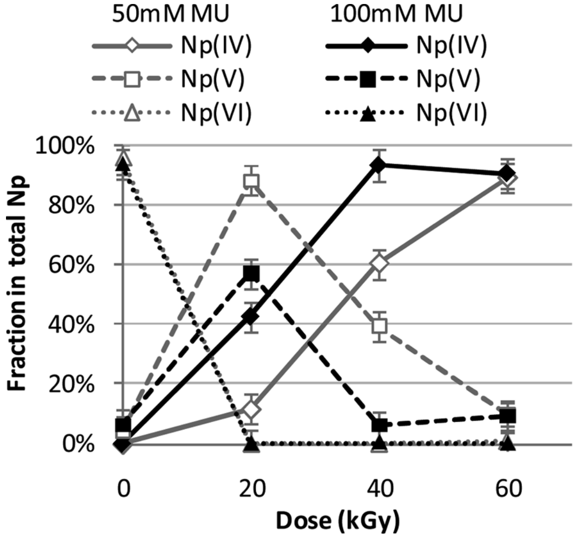

FIG. 8. Dose dependent change of redox speciation of 1.3 mM Np in aq. 4 M HNO_3 irradiated solutions containing 50 mM and 100 mM methylurea; For the non-replicate measurements, a ±5% error associated with the spectrophotometric measurements is indicated.

The reason for the next reduction step, from Np(V) to Np(IV), is less understood. The reduction more likely proceeds as a result of further reduction of Np(V) by accumulated H_2O_2, as the progress of the complete reduction of Np(V) to Np(IV) by H_2O_2 has been observed in solutions with HNO_3 concentrations greater than 4 M concentration (15). Another possible mechanism contributing to reduction would be Np(V) disproportionation to Np(VI) and Np(IV), followed by reduction of Np(VI) by H_2O_2 (16). Additionally, the radiolytic oxidation of Np(IV) to Np(V) and Np(VI) in solutions of 1–6 M HNO_3 was reported (17), and the primary oxidizing agent of Np(IV) was attributed to NO_3 radicals; hence, additional research is needed to explain why the effect of Np(IV) oxidation by $NO_3\cdot$ is overcome by the reduction of Np(V) in the absence of HNO_2 and presence of H_2O_2 in concentrated nitric acid solutions.

CONCLUSION

In solutions of 4 M HNO_3, acetamide (1–15 mM) does not efficiently scavenge nitrous acid. Experiments performed with methylurea (1–500 mM) indicate that doses of 40–60 kGy result in degradation of methylurea at concentrations lower than 50 mM, with radiation yield of 7–8 mM/kGy.

Attempts to prevent the radiolytic reduction of Np(VI) to Np(V) by additions of 1–10 mM methylurea and 1–10 mM vanadium(V) as a holding oxidant were unsuccessful. More than 50% of the Np(VI) was reduced to Np(V), which would be problematic for UNF reprocessing since Np(V) is poorly extracted by TBP. Unexpectedly, the radiolytic reduction of Np(VI) was promoted with additions of higher concentrations of methylurea (50 and 100 mM). With a dose of 60 kGy, about 90% of Np existed as the tetravalent oxidation state. This is likely caused by scavenging the nitrous cid by MU, which permits an increase of H_2O_2 concentration. Hence, high concentrations of MU did not prevent Np(VI) reduction; however, this could have a positive practical implication during the solvent separation process because Np(IV) is also well extracted by TBP. Nonetheless, application of MU has to be experimentally verified since the scavenging of HNO_2 by MU appears to significantly alter the redox processes during nitric acid radiolysis. In perchlorate media it was observed that Np(IV) may act as a reducing agent for Pu(IV)(18). These effects may adversely affect the extractability of plutonium, since Pu(III) is very poorly extracted by TBP.

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