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Neptunium_Oxide_Precipitation_Kine

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Neptunium oxide precipitation kinetics in aqueous systems at elevated temperatures, Part I: Colloidal, temperature, inert atmosphere, and ionic strength measurements

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Summary. We evaluate the proposed NpO_2^+(aq)-NpO_2(cr) reduction-precipitation system at elevated temperatures to obtain primary information on the effects of temperature, ionic strength, O_2 and CO_2. Experiments conducted on unfiltered solutions at 10^{-4} M NpO_2^+(aq), neutral pH, and 200°C indicated that solution colloids strongly affect precipitation kinetics. Subsequent experiments on filtered solutions at 200, 212, and 225°C showed consistent and distinctive temperature-dependent behavior at reaction times $\leq$ 800 hours. At longer times, the 200°C experiments showed unexpected dissolution of neptunium solids, but experiments at 212°C and 225°C demonstrated quasi steady-state neptunium concentrations of 3×10^{-6} M and 6×10^{-6} M, respectively. Solids from a representative experiment analyzed by X-ray diffraction were consistent with NpO_2(cr). A 200°C experiment with a NaCl concentration of 0.05 M showed a dramatic increase in the rate of neptunium loss. A 200°C experiment in an argon atmosphere resulted in nearly complete loss of aqueous neptunium. Previously proposed NpO_2^+(aq)-NpO_2(cr) reduction-precipitation mechanisms in the literature specified a 1:1 ratio of neptunium loss and H^+ production in solution over time. However, all experiments demonstrated ratios of approximately 0.4 to 0.5. Carbonate equilibria can account for only about 40% of this discrepancy, leaving an unexpected deficit in H^+ production that suggests that additional chemical processes are occurring.

Introduction

Of the long-lived actinides, ^{237}Np ($t_{1/2} = 2.14\times10^6$ y) poses a particular set of challenges to used nuclear fuel repository evaluations. While it represents a small fraction of the total radioactivity of used fuel, ^{237}Np is a primary dose contributor in a used fuel repository between 10^4 and 10^6 years after fuel irradiation [1]. The ^{237}Np concentration in used fuel increases over the first 4,300 years after irradiation due to the decay of ^{241}Pu ($t_{1/2}$ = 14.4 y) and ^{241}Am ($t_{1/2}$ = 432.7 y) [2]. Additionally, neptunium chemistry differs from that of its nearest neighbors (uranium and plutonium) in that it is generally dominated by the (5+) oxidation state under common environmental conditions, making it more soluble and less likely to sorb onto repository host materials [3]. It is essential, therefore, to understand the chemical behavior of neptunium in a repository environment, including its likely dissolution mechanisms from used fuel, aqueous

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oxidation states, and precipitation behavior to determine the likelihood of neptunium migration in the biosphere and, if necessary, to develop methods to retard its movement.

Several studies have examined aqueous $NpO_2^+(aq)$ systems under near neutral conditions to determine the solubility-limiting solids that will control neptunium behavior over long time scales; a detailed summary can be found in Roberts et al. [4]. Briefly, two independent research groups [5–9] conducted solubility studies in near-neutral Yucca Mountain ground waters from oversaturation with the $NpO_2^+(aq)$ ion at temperatures of 25, 60, and 90°C. They identified solid phases as $Na_xNpO_2(CO_3)_x \cdot xH_2O$ and $Np_2O_5 \cdot xH_2O$ and demonstrated solubilities in the range 5×10^{-6} to 6×10^{-3} M that raised estimated neptunium releases from a repository by several orders of magnitude compared to the solubilities determined from spent fuel leaching tests [10–12].

Another research group [13] used the chemical thermodynamic modeling program EQ3/6 to model $NpO_2^+(aq)$ solubility under the experimental conditions like those in [5–9] and found that the model did not predict the $Na_xNpO_2(CO_3)_x \cdot xH_2O$ or Np_2O_5 neptunium(V) solids or the high solubilities. Rather, the model suggested that those solutions were "grossly saturated with respect to NpO_2", according to Eq. (1). The authors surmised that the formation of the more thermodynamically stable solid $NpO_2(cr)$ might be kinetically hindered, and that the month- to year-long times scales of previous experiments had been inadequate to allow $NpO_2(cr)$ formation.

$$NpO_2^+(aq) + \tfrac{1}{2}H_2O \Leftrightarrow NpO_2(s) + H^+ + \tfrac{1}{4}O_2 \qquad (1)$$

Roberts et al. [4,14] sought to test this kinetic limitation hypothesis by conducting $NpO_2^+(aq)$ solubility experiments in dilute chloride media at elevated temperatures to accelerate the reaction kinetics. The initial neptunium concentration in the solutions was 10^{-4} M neptunium, low enough to prevent the precipitation of various neptunium(V) solids at room temperature. The initial solutions were at near-neutral pH and were equilibrated with air. After heating at 200ºC, solid material precipitated in both Teflon-lined stainless steel vessels and unlined, passivated titanium vessels. The precipitated solids were found to have structures consistent with $NpO_2(cr)$ via XRD, EXAFS, and XANES. Additionally, other studies [15,16] have examined the formation of neptunium(IV) phases within uranium-bearing solids at similarly elevated temperatures of 90 and 150ºC. Using XRD, SEM, TEM, and EELS, these neptunium phases were shown to be consistent with distinct crystalline NpO_2 and Np_2O_5 phases within the larger, oxidized uranium matrix, showing similar neptunium precipitation behavior to that noted by Roberts et al. [4].

The study presented here was undertaken to confirm the initial findings of Roberts et al. [4] and to examine the first-order effects of temperature, ionic strength, O_2 and CO_2 on the kinetics and solubilities of the proposed $NpO_2^+(aq)$-$NpO_2(cr)$ reduction-precipitation system (Eq. (1)).

Materials and Methods

A 1.7 g neptunium foil with an unknown history was treated with several drops of HNO_3 to dissolve the outer, passivated oxide layer. The remainder of the foil was dissolved in approximately 200 mL of 6 M HCl. Approximately 50 mg of neptunium at a time were removed from the resulting dark emerald green solution and were purified via ion exchange after reduction of NpO_2^+ to Np^{4+} with HI. The effluents were then heated to dryness in 2 M HNO_3 to remove any residual iodide, oxidizing the neptunium to NpO_2^{2+}. The dry residue was dissolved in a few milliliters of 1 M HCl, and several drops of 3% H_2O_2 were added to reduce NpO_2^{2+} to NpO_2^+ [17]. A purified stock solution of NpO_2^+ chloride media was prepared by precipitation of $NpO_2OH(am)$ via NaOH addition, the precipitate rinsed three times with DI water, and the remaining solid dissolved in a minimum of 0.1 M HCl [18,19]. The resultant neptunium concentration was determined via low-energy photon spectrometry (LEPS) using the 29.374-keV gamma-ray and the oxidation state was confirmed as NpO_2^+ with UV/Vis spectrophotometry (Guided Wave Model 260) [20].

Twelve titanium pressure vessels (Parr Instrument Company, model 4750) passivated with nitric acid were used for all experiments in this work. Initial experiments were performed as noted in Roberts et al. [4]: 80 mL of water (distilled, Milli-Q Plus Water System) were added to a clean titanium reaction vessel. Approximately 1 mL of the purified Np(V) stock solution was added to obtain a neptunium concentration of about 10^{-4} M, verified via LEPS, and the solution pH was measured (Thermo Electron Corporation, model 8130) and adjusted to approximately pH 6 with 0.05 M HCl or 0.05 M NaOH,. The concentrations of Na^+ and Cl^- were also measured for some solutions (Thermo Electron Corporation, Orion 86-11 and 96-17, respectively) to determine the overall ionic strength of the solution and to detect any gross pH electrode solution leakage over time. During preparation activities, the experimental solutions were allowed to equilibrate with the atmosphere for tens of minutes to several hours and the solutions were well mixed to ensure homogeneity. The prepared vessels were sealed and allowed to react in a pre-heated laboratory oven (VWR, model 1410MS).

At varying time intervals, the vessels were removed from the oven and allowed to cool for 1.5 to 3 hours. The vessels were unsealed, sampled for total aqueous neptunium concentration and measured for pH. Neptunium samples were taken along the centerline of the vessel and approximately one to two centimeters below the solution surface. Samples were filtered with a 30,000 molecular weight cut-off polysulphone filter (Whatman, Model 6835-3001); 0.5 mL of solution was filtered and discarded, followed by 0.5 to 2 mL of solution filtered for LEPS counting. The pH electrode was also inserted along the centerline of the vessel, but was immersed to about 2.5 cm above the vessel floor. The vessels experienced some mild agitation as they were removed from the oven and opened, but no concerted effort to stir the solutions was made, before or after measurement. After sampling, the vessels were resealed and placed back in the pre-heated oven to continue reacting at temperature.

After some initial experiments showed significant inconsistencies in the rate of neptunium loss from solution, it was suspected that colloidal material in the initial solutions was influencing the apparent neptunium precipitation kinetics. As a result, all solutions used in subsequent experiments were filtered with 20 nm Anopore filters (Whatman) and checked for particulate matter using a 90Plus Particle Size Analyzer (Brookhaven Instruments Corporation). Reaction vessels were rinsed with filtered water 10 to 15 times to remove gross particulate matter.

To quantify the significant effects that oxygen and carbon dioxide can have on this chemical system, an experiment was prepared with unfiltered solutions to the usual 10^{-4} M $NpO_2^+(aq)$ concentration and a starting pH of 6, but was made in an argon atmosphere glove box with a measured O_2 concentration of 3 to 8 ppm and with water that was distilled under argon to be as carbonate-free as possible. All neptunium assays and pH measurements were made in the argon atmosphere glove box.

To evaluate the significance of ionic strength on the chemical system, an experiment was conducted in unfiltered solutions with the usual 10^{-4} M neptunium starting concentration and a starting pH of 6.2, but was made with a solution of 0.05 M NaCl to raise the ionic strength by at least an order of magnitude compared to the other experiments reacted at the same temperature.

Three experiments were performed without neptunium present in order to determine the effect of the titanium vessels walls on the pH of the experimental solutions. The first experiment was performed in a vessel whose interior surface had been oxidized with 1 M HNO_3 at 200°C for two days, which produced a thin, white film on the vessel surface that was easily removed by rinsing with water. This oxidation process was performed to determine if a presumed thicker titanium oxide layer had any effect on solution pH behavior. The second and third experiments were performed in titanium vessels that were cleaned according to the standard procedures. All three experiments were prepared in the same way as the filtered neptunium experiments, but without neptunium. Two experiments, including the over-oxidized vessel, were adjusted to a starting pH of 6, and one experiment was adjusted to a starting pH of 4.5, after which they were allowed to react at 212°C.

Neptunium solids were harvested from the experimental solution and the vessel floor via centrifugation of the remaining solution at the termination of an experiment, as well as from solids scraped from the vessel walls with a plastic instrument. To examine the distribution of solids on the vessel walls at the termination of an experiment, three reacted vessels were emptied of solution, allowed to air dry, and placed in a "down-looking" gamma-ray counter to measure the intensity of the 29.374-keV gamma-ray from the decay of ^{237}Np. The vessels were then removed from the counter, fitted with a 1-mm thick copper disk that covered the floor of the vessel, and returned to the counter to repeat the measurements. The copper disk attenuates the 29.374-keV gamma-ray emission from any neptunium attached to the vessel floor, allowing for an evaluation of the distribution of the precipitated neptunium solids on the vessel walls versus the vessel floor. X-ray diffraction measurements of a representative sample were performed at the University of Nevada, Las Vegas using a PANalytical X'Pert PRO Multi-Purpose Diffractometer.

Results and Discussion

Unfiltered solutions at 200°C (0 ≤ t ≤ 800 hours)

The first experiment used unfiltered DI Milli-Q water and was performed in triplicate in an effort to replicate and confirm the results from Roberts et al. [4] at 200°C. Differences in the aqueous neptunium and hydrogen ion concentrations between the two data sets appear at the first measurements taken at approximately 200 hours, where the unfiltered experiments (Fig. 1, solid shapes) experience a more rapid loss of aqueous neptunium than those reported by Roberts et al. [4] (Fig. 1, open triangles). The data from the three unfiltered experiments also show variations in neptunium concentration by a factor of about 2. This variation continues throughout almost 4500 hours of reaction time (Fig. 2), and all three had long-term aqueous neptunium concentrations lower than those reported by Roberts et al. [4]. Both the deviation from the Roberts data and the differences in neptunium concentration between the three identically prepared experiments suggested that some other constituent in the solutions, such as dust or colloidal particles, or differences in the titanium vessel surfaces, might have influenced the precipitation behavior of the neptunium.

The unfiltered experiments from this work also show a change in the hydrogen ion activity over time that is unexpected given the 1:1 relationship between neptunium ion loss and hydrogen ion gain predicted by Eq. (1). For ease of further discussion, we define this relationship as shown in Eq. (2), where *i* is the initial measured value taken at time zero, and *j* is the measured value at a given *j* hours of reaction time.

$$d\{H^+\}\big/d\left[Np_{(aq)}\right]=\left|\frac{\{H^+\}_j-\{H^+\}_i}{\left[Np_{(aq)}\right]_j-\left[Np_{(aq)}\right]_i}\right| \qquad (2)$$

The comparison of the j^{th} $\{H^+\}$ and $[Np_{(aq)}]$ measurements to those at the experiment initiation is preferred to a comparison of the j^{th} and $(j-1)^{th}$ values. As these experiments progress, the change in $[Np_{(aq)}]$ from measurement to measurement typically becomes very small compared to the j^{th} and $(j-1)^{th}$ $\{H^+\}$ change. Because of this, any small errors in pH measurement (which has a consistent ±0.02 pH unit error across this pH spectrum) can drastically skew the $d\{H^+\}/d[Np_{(aq)}]$ comparison from one measurement to another and generates very large error bars. The relationship given by Eq. (2) provides an integral accounting of the $d\{H^+\}/d[Np_{(aq)}]$ behavior over time with small errors. While the $\{H^+\}$ in these unfiltered solutions increases with each decrease in measured aqueous neptunium concentration, the values for $d\{H^+\}/d[Np_{(aq)}]$ at the end of these unfiltered experiments (Fig. 2) are 0.55 (solid circles), 0.56 (solid diamonds), and 0.47 (solid squares), half of that expected from Eq. (1), again indicating possible interference from colloids, interactions with the vessel walls or precipitation along with counter ions.

Filtered solutions at 200 °C ($0 \leq t \leq 800$ h)

Additional experiments were then performed in triplicate under the same conditions at 200°C but using DI Milli-Q water filtered with 20 nm Anopore filters. Data for these experiments at short times are also shown in Fig. 1 (open shapes). These filtered solutions show two significant features when compared to the unfiltered experiments: (1) a more consistent total aqueous neptunium concentration between replicate experiments, especially for the first 200 hours of reaction time, and (2) a possible change in the rate of neptunium loss from solution occurring at 12 hours of reaction time elucidated by additional sampling at very early reaction times. All three of these filtered solutions demonstrate a continuous increase in $\{H^+\}$, but show $d\{H^+\}/d[Np_{(aq)}]$ values of 0.58 (open circles), 0.28 (open diamonds), and 0.45 (open squares) after 765 hours.

Filtered experiments at 200 °C at ($800 \leq t \leq 11051$ h)

The filtered experiments at 200°C were allowed to continue for an additional 10,251 hours of reaction time, shown in Fig. 2 with long term data from Roberts et al. [4] and the unfiltered experiments from this work for comparison. After closely following the aqueous neptunium concentration behavior reported by Roberts et al. [4] for the first 1000 hours of reaction time, the filtered experiments demonstrate an increased rate of aqueous neptunium loss from approximately 1000 to 3000 hours of reaction time, during which all three filtered experiments reached an aqueous neptunium concentration of approximately 3×10^{-6} M. A more rapid decrease in neptunium concentration for all three filtered experiments, but especially the one noted by open circles, can be seen at about 1000 hours. After approximately 3000 hours of total reaction time, however, all three filtered experiments experienced a sudden and unexpected order of magnitude increase in neptunium concentration and a decrease in $\{H^+\}$. The neptunium in solution began to decrease again after approximately 4500 hours of total reaction time, although assays taken at 8,771 and 11,051 hours also show erratic behavior.

The rapidity of the decrease in aqueous neptunium concentration near 1000 hours initially suggested an experimental cause, possibly a solution contamination from a leaky pH electrode. Thus, no pH measurements were taken between 1094 and 2911 hours total reaction time in order to preclude any further potential solution contaminations. After that initial drop in aqueous neptunium, the neptunium behavior quickly became more consistent between experiments and continued its more measured loss from solution. It was surprising, then, to discover the subsequent jump in neptunium concentration that begins near 3000 hours in all three experiments, especially as no pH measurements were being taken, removing any obvious sources of solution contamination. pH measurements were resumed after the spike in aqueous neptunium concentrations in order to better monitor solution conditions. Notably, the hydrogen ion activity in solution dropped as neptunium concentration increased, which does follow the general relationship predicted by Eq. (1). However, as with measurements taken at shorter reaction times (>800 h), the final values for $d\{H^+\}/d[Np_{(aq)}]$ are less than half of those expected from Eq. (1): 0.41 (open circles), 0.30 (open diamonds), and 0.47 (open squares). Fig. 3 shows the change in the $d\{H^+\}/d[Np_{(aq)}]$ ratio over time for the unfiltered and filtered experiments at 200°C, as well as those from Roberts et al. [4]. Two of the filtered experiments at 200ºC (open diamonds and open squares) show an initial $d\{H^+\}/d[Np_{(aq)}]$ ratio that is quite low and increases to approximately 0.4 after 200 hours. One filtered experiment at 200ºC (open circles) demonstrates early variation and a higher $d\{H^+\}/d[Np_{(aq)}]$ ratio closer to 0.5. All three filtered experiments at 200°C show distinct variations and very low $d\{H^+\}/d[Np_{(aq)}]$ ratios between 1000 and 11,051 hours, indicating that another reaction other than Eq. (1) may have a controlling influence on neptunium and hydrogen in solution.

The role of carbonate in experimental solution behavior

While the elimination of colloids >20 nm appeared to provide much more consistent neptunium precipitation behavior, especially at short times, it played no significant role in the $d\{H^+\}/d[Np_{(aq)}]$ ratio behavior. To further explore the potential reasons behind these unexpected $d\{H^+\}/d[Np_{(aq)}]$ ratios in the experiments in the previous sections, we investigated the potential influence of carbonate on the experimental systems. The carbonate equilibrium shown in Eq. (3) has an influence on most near-neutral chemical systems in equilibrium with the atmosphere.

$$CO_2(g) \Leftrightarrow CO_2(aq) + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-} \qquad (3)$$

While our experimental solutions are closed systems isolated from the atmosphere while at elevated temperatures, they are open to the atmosphere at room temperature during preparation and sampling activities. To conservatively estimate the effect that carbonate has on a typical experiment, we use one of the filtered experiments at 200ºC as an example (open squares in Fig. 2). Using the experimental starting parameters of $[Np_{(aq)}] = 1.04\times10^{-4}$ M and a pH of 6.61, final solution parameters of 4.97×10^{-6} M aqueous neptunium and a pH of 4.33, along with well-known Henry's Law and equilibrium constants [21], the estimated concentration of bicarbonate and carbonate species are shown in Table 1. Clearly, the only notable $\{H^+\}$ sink present is the $[HCO_3^-]$ in solution. As the reduction-precipitation reaction (Eq. (1)) is occurring, the $\{H^+\}$ content rises, causing the equilibrium of Eq. (3) to shift to the left, consuming some of the $\{H^+\}$ produced; when a experimental vessel is opened for measurement, the solution re-equilibrates with the atmosphere, expelling CO_2(g), and slightly less carbon is available in the system. From these simple estimates, it appears that the maximum $\{H^+\}$ lost to the carbonate equilibrium is approximately 2×10^{-5} M. In most of the experimental solutions thus far, approximately 5×10^{-5} M of hydrogen ion activity or more are unaccounted for. This suggests that, beyond the carbonate equilibria in Eq. (3) and the neptunium reduction via water in Eq. (1), at least 25% of the expected $\{H^+\}$ is consumed by some other mechanism or is not produced in the first place due to an alternate or competing mechanism.

Table 1: Estimated concentrations of solution constituents at initial and final times

Species	Estimated Initial Concentration, M	Estimated Final Concentration, M
CO_2(aq)	1.25×10^{-5}	1.25×10^{-5}
HCO_3^-	2.25×10^{-5}	1.18×10^{-7}
$NaHCO_3$	2.34×10^{-12}	1.23×10^{-14}
$NpO_2CO_3^-$	2.38×10^{-8}	5.40×10^{-14}
CO_3^{2-}	4.30×10^{-9}	1.19×10^{-13}
NpO_2OH(aq)	1.59×10^{-9}	5.33×10^{-13}

Unfiltered solution at 200 °C in an argon atmosphere

To complement our carbonate calculations, an experiment was conducted under an argon atmosphere to evaluate the effect of an absence of carbonate and oxygen on our reduction/precipitation system. As shown in Fig. 4, the experiment behaved almost identically to the 200°C experiments conducted in air for the first 1000 hours of reaction time. By almost 1500 hours, however, the aqueous neptunium concentration had plummeted to or below the ^{237}Np detection limit of the LEPS (approximately 10^{-9} M ^{237}Np), making the final data point an estimate with a high degree of uncertainty. The hydrogen ion behavior for this experiment (Fig. 4) was almost identical to those measured for filtered experiments at 200°C for the entire 1500-hour reaction time, with a final $d\{H^+\}/d[Np_{(aq)}]$ of 0.56; this ratio was very consistent at each measurement throughout the experiment (Fig. 6). These findings further indicate that some additional chemical mechanism is occurring outside those predicted by Eq. (1) and Eq. (3).

Filtered experiments with no neptunium at 212 °C

Because colloids and the carbonate equilibria did not seem to be the controlling factor in the d$\{H^+\}$/d$[Np_{(aq)}]$ ratio, we conducted experiments to elucidate the role of the passivated titanium vessel surfaces with respect to the experimental solutions. One experiment without neptunium started at pH 4.5 showed no significant pH deviation throughout the entire 150 hours of reaction time. The filtered experiment in the non-over-oxidized vessel begun at pH 5.85 experienced a small change to pH 5.68. The solution in the over-oxidized vessel with a starting pH of 5.96 showed an order of magnitude increase in hydrogen ion concentration to pH 4.90 during the first 40 hours of reaction time.

These three experiments demonstrate two important titanium vessel characteristics. The first is that they do not have a negative impact on the hydrogen ion content in solution and are therefore unlikely to be a substantial hydrogen sink. The second vessel characteristic is that there may or may not be a moderate amount of hydrogen ion production caused by the vessel, but even at its highest level (~10^{-5} M for the over-oxidized vessel), it is still below that recorded for a typical neptunium reduction reactions (~4×10^{-5} M). However, these simple experiments do not rule out the possibility for the vessel surfaces to influence the aqueous neptunium concentration of the experimental solutions by acting as NpO_2^+ adsorption sites.

Unfiltered solution at 200 °C at increased ionic strength

The ionic strength of a solution can have a significant effect on precipitation behavior. The difference between this experiment at an ionic strength of approximately 0.05 M (Fig. 5), and the experiments at lower ionic strength was striking: the aqueous neptunium concentration dropped by almost two orders of magnitude within the first 48 hours of reaction time, to approximately 3×10^{-6} M, approximately four times faster than similar solutions at ionic strengths of about 2×10^{-3} M. A subsequent order of magnitude increase took place over the next 500 hours, but was followed by a second drop in neptunium concentration before rebounding to a steady state of ~10^{-5} M aqueous neptunium, similar to the steady state neptunium concentrations seen in the lower ionic strength experiments at 200°C at long reactions times (Fig. 2).

There are two items of note regarding the hydrogen ion activity during this experiment. First, after increases in $\{H^+\}$ while $[Np_{(aq)}]$ decreased for the first 500 hours, the $\{H^+\}$ responded in the exact opposite manner when there was a measured drop in aqueous neptunium at 734 hours. Second, there was a distinct difference in the d$\{H^+\}$/d$[Np_{(aq)}]$ ratio before and after this unexpected event. Before the drop in $\{H^+\}$ and $[Np_{(aq)}]$, the d$\{H^+\}$/d$[Np_{(aq)}]$ ratio was approximately 0.75, and after it was approximately 0.35 (Fig. 6). We know of no experimental reason for such a sudden shift in experimental parameters.

Because of the profound differences in neptunium and hydrogen ion behavior seen in this raised ionic strength experiment, it was decided to measure the background electrolyte concentrations in other, lower ionic strength experiments, especially given their sometimes erratic neptunium concentration behavior. Briefly, experiments measured at preparation had typical ionic strengths on the order of 0.2 mM and those measured after reaction times between 3,000-11,000 hours had 1 to 2 mM total ionic strength. These changes do not demonstrate any obvious correlation to neptunium or {H+} behavior, including the filtered experiments at 200ºC that show such erratic behavior at long reaction times.

Filtered experiments at 200, 212, and 225 °C ($t \leq 300$ h)

After the filtered experiments at 200°C showed a significant improvement in the consistency of the aqueous neptunium measurements at early times, two additional sets of triplicate experiments were prepared in the same manner and allowed to react at 212°C and 225°C (Fig. 6; data from 200°C filtered experiments included for comparison). Although the neptunium measurements within each temperature set begin to show some variations as the experiments progress, they are reasonably consistent within each temperature group. At times less than about 100 h, the neptunium concentrations show markedly different loss rates that increase with increasing temperature. At times between 100 h and 300 h, the loss rates decrease significantly and appear to have similar time dependencies.

Filtered experiments at 200, 212, and 225 °C (all times)

The filtered, low ionic strength experiments conducted at 200, 212, and 225°C continued to react for a total of approximately 11,000, 6,000, and 4,000 hours, respectively. The results for all of the aqueous neptunium and hydrogen ion activity measurements for these experiments are shown in Fig. 7. Three trends appear in these data. (1) The three sets of experimental data show well-defined, monotonic decreases in aqueous neptunium concentrations until approximately 3000 hours of reaction time, with the exception of one experiment at 225°C. The slope of the data during this time period shows marked temperature dependence. (2) From approximately 2000 to 4000 hours, there appears to be a temperature dependence on the quasi steady-state aqueous neptunium concentrations for experiments at 212°C and 225°C. The experiments at 200°C experienced dissolution and increased aqueous neptunium concentrations before reaching any sort of steady state behavior as discussed above. However, from the 212°C and 225°C experiments, it appears that the aqueous neptunium solubility increases with increasing temperature. (3) Each set of experiments had at least one vessel that showed dissolution and re-precipitation behavior at longer times. The extent of the dissolution varied significantly, by up to an order of magnitude.

The hydrogen ion activity for the filtered experiments at 212 and 225°C showed clear consistency within each temperature group (Fig. 7), especially at short times (Fig. 6). The $d\{H^+\}/d[Np_{(aq)}]$ relationship for these experiments (Fig. 6) are also fairly consistent: they are initially low, approximately 0.3 to 0.4, and quickly increase to quasi-steady-state values of approximately 0.45 to 0.5. These changes in the $d\{H^+\}/d[Np_{(aq)}]$ over time mirror that of the overall $[Np_{(aq)}]$ loss at the very beginning of each experiment, indicating that, not only might there be additional chemical processes occurring besides those shown by Eq. (1) and Eq. (3), but also that the alternate mechanism may dominate at early times ($t < 500$ hours).

While all three sets of these filtered experiments have at least one solution with variable or erratic behavior at long times, their overall ionic strengths are at least 20 times lower than in the 0.05 M NaCl experiment. Additionally, the variant experiments at 212 and 225°C do not seem to correlate to any particular ionic strength value, although measurements at 212°C were only taken at the experimental outset, so long-term ionic strength information is unavailable.

Solids analysis

The comparison of the three reaction vessels counted with and without the copper shield on the vessel floor confirmed visual observations: the data are consistent with a quasi-uniform deposition of neptunium on the vessel surfaces that were in contact with the solutions. The experimental neptunium solutions were in contact with both the vessel floor and approximately two thirds of the surface area of the vessel walls; the ratio of the available wall surface area to the total available surface area of the vessel walls and floors together is 0.88. The ratios of the neptunium detected with the vessel floor covered and with the floor uncovered for the three analyzed vessels were 0.928, 0.956, and 0.879. These measurements correspond quite well to the expected ratio of 0.88, indicating that the solid neptunium is associated with the vessel walls in a uniform manner. However, it does not indicate when in the reduction/precipitation process the neptunium became associated with the vessel surfaces; the $NpO_2^+(aq)$ ion may migrate to the vessel walls, where it is then involved in reduction and precipitation reactions, or the $NpO_2^+(aq)$ ion may be reduced and precipitated in solution (either homogeneously or in association with colloidal material) and then migrate to the vessel walls.

Solids were harvested from all of the reaction vessels and had a consistent appearance throughout all experiments. X-ray diffraction (XRD) analysis was performed on the solid material collected from the experiment at 225°C shown by solid circles in Fig. 6 and Fig. 7 as a representative sample. The measured spectrum is shown in Fig. 9. The database of diffraction patterns that accompanies the Panalytical X'Pert Pro diffractometer identified every measured peak as belonging to crystalline, cubic NpO_2; no extraneous peaks beyond those expected for $NpO_2(cr)$ were found. The software also calculated a cubic lattice parameter of 5.4319 ± 0.0001 Å, which is slightly different than the published values of 5.426 Å from similar experiments (at a slightly lower temperature and with a shorter reaction time) from Roberts et al. [4] and of 5.434 Å for anhydrous NpO_2(cr) [21]. An experimentally determined density of 11.1907 ± 0.0006 g/cm^3 [4] also differs slightly from the literature value of 11.14 g/cm^3 [21]. While the crystalline material in the measured sample is consistent with NpO_2, X-ray diffraction techniques cannot easily detect truly amorphous or micro-crystalline materials. Thus, the solid sample may in fact contain amorphous neptunium solids in addition to the identified NpO_2(cr).

Discussion of results

One of the most important findings of this work is that the quasi steady state neptunium solibilities for the filtered experiments at 212 and 225ºC are approximately 4×10^{-6} and 7×10^{-6} M, two to three orders of magnitude lower than the neptunium solubilities determined for precipitated neptunium (V) solids in repository waters at similar final pH values. This indicates that the current estimates for neptunium migration in a repository setting may be overestimated.

The experimental data presented in this work demonstrate several other noteworthy behaviors, particularly within the context of recent scholarship on actinide (IV) solid phases and solubilities. (1) The experiments show a distinct temperature dependence on kinetics at short times; kinetic rates seem to be only slightly temperature dependent at long times. (2) Many of the individual experiments show variable solubility over time, up to an order of magnitude. (3) All experiments showed $d\{H^+\}/d[Np_{(aq)}]$ ratios of approximately 0.5, rather than unity, as predicted by Eq. (1). Carbonate equilibria can account for, at most, half of this discrepancy. Additionally, most experiments demonstrated a lower $d\{H^+\}/d[Np_{(aq)}]$ ratio at short times when the temperature dependent kinetics are dominant. (4) The passivated titanium reaction vessels are not hydrogen ion sinks, but may be a small to moderate hydrogen ion source. (5) The solid material harvested from a representative sample is consistent with known XRD spectra from NpO_2(cr), but the measured lattice parameter is slightly different from literature values for high-fired, anhydrous NpO_2(cr). XRD analysis would not have identified any amorphous solid phases.

All of these behaviors indicate that an alternate mechanism is present besides the neptunium reduction by water (Eq. (1)) and the carbonate equilibrium with the atmosphere (Eq. (3)).Recent scholarship on the actinide (IV) dioxides and solubility-controlling oxide and oxyhydroxide solids [22,23] may help to evaluate the neptunium behavior seen in this work. Much of the thermodynamic data for actinide (IV) dioxide behavior in contact with aqueous solution has been conducted on high-fired (> 800°C), well-characterized anhydrous dioxides. The solid phases produced in this work and by Roberts et al. [4] from oversaturation at temperatures ≤ 225°C most likely contain waters of hydration to varying degrees, as well as some amorphous material. The size (and therefore solubility) of any precipitated neptunium oxide crystalline material most likely varies significantly over time as well [24]. Indeed, the bulk composition and crystalline surfaces of any precipitated material may also vary in composition, as has been indicated for AnO_2(cr) where An = Th, U, Np, and Pu [25]. Both of these factors may contribute to the erratic behavior in several experiments, and to the large differences in the expected versus measured d$\{H^+\}$/d[$Np_{(aq)}$] ratios.

A number of studies have recently suggested that certain plutonium oxides, in particular the “colloidal” form of plutonium, may have previously unknown solids structures. First is the proposed existence and characterization of PuO_{2+x} (where $x \leq 0.25$) [26–28], thought not to exist until recently. One key finding about this oxide structure is that, because the X-ray scattering in these solid phases is dominated by plutonium, whose lattice positions remain consistent despite the addition of oxygen to the system, the changes in the oxygen content are almost undetectable via XRD. In fact, the variation in the PuO_{2+x} lattice parameter from $2.0 \leq x \leq 2.25$ is a_o(Å) = 5.3643 + 0.01746 O:Pu [26]. The deviation from PuO_2 to $PuO_{2.25}$ of only +0.004365 Å is on the same order of magnitude as the differences in experimentally measured lattice parameters from this work and from Roberts et al. [4] compared to literature values [21] for anhydrous NpO_2(cr): -0.0021 Å and -0.008 Å, respectively. Additionally, while the plutonium lattice expands slightly with oxygen incorporation, the UO_2 lattice is known to shrink under the similar processes. While the differences in measured neptunium oxide lattice parameters may be an insignificant anomaly, it is possible that neptunium dioxides may undergo similar alterations as UO_2 or PuO_2 when exposed to H_2O and O_2 environments. The second recent development is the characterization of plutonium in the “colloidal” form as actually plutonium oxide nanoclusters with the structure $[Pu_{38}O_{56}Cl_{54}(H_2O)_8]^{14-}$, with an oxygen deficient $[Pu_{38}O_{56}]^{40-}$ cluster and charge balancing chloride ions and water molecules [29]. While there is currently no evidence for such solids in neptunium(IV) oxide solids formed in aqueous solutions, these kinds of alternate plutonium structures raise the possibility of related neptunium solids that may provide pathways for additional neptunium-related chemical processes occurring in our experimental solutions beyond that specified by Eq. (1).

Conclusions

We present detailed studies of the kinetics of neptunium reduction and precipitation at elevated temperatures for a variety of experimental variables. Although the previously proposed reaction (Eq. (1)) does not completely describe the processes occurring in these solutions, we show that some combination of processes, or an “effective” set of neptunium reactions is heavily influenced kinetically by temperature especially at short reaction times, the absence of oxygen and carbonate, and the ionic strength of the solution, and displays evidence of solid phase ripening over time. The modeling of suggested mechanisms for these reactions will be presented in a subsequent paper. Most importantly, the quasi steady state solubilities for these reactions near pH 4 to 4.5 are two to three orders of magnitude lower than those found for neptunium (V) solids precipitated at lower temperatures, indicating that current estimate for neptunium migration in a repository setting may be overestimated. Much remains to be investigated, however, including monitoring the role of other redox species in solution, solids analyses to further probe the structure of the precipitated solids, and research on NpO_2(cr) and its proclivities for additional phases and their characteristics.

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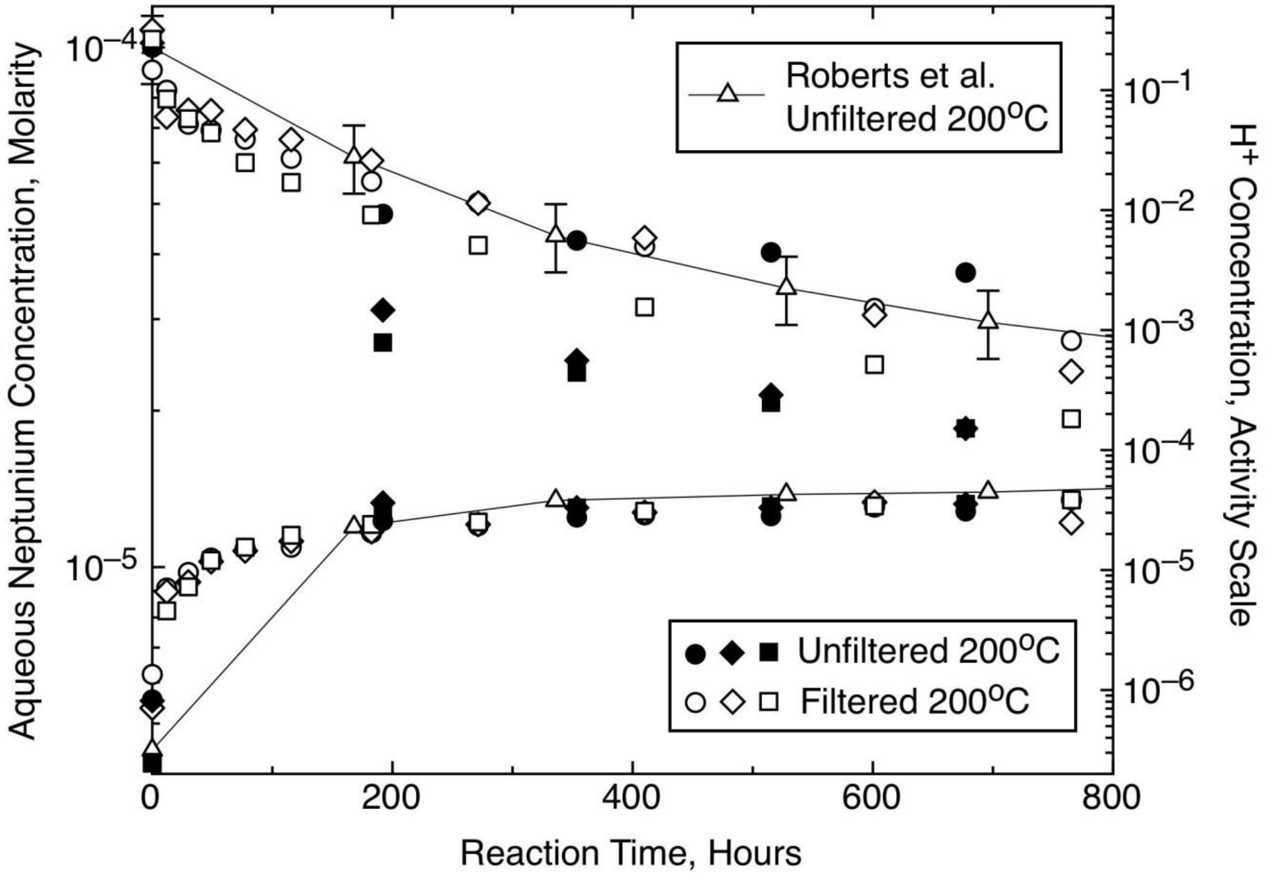

Fig. 1. Aqueous neptunium concentrations and hydrogen ion activities from NpO_2^+ precipitation experiments at 200°C using unfiltered solutions from Roberts et al. [4] and this work, and filtered solutions from this work at short times. Data in the top half of the figure use the left ordinate; data at the bottom of the figure use the right ordinate.

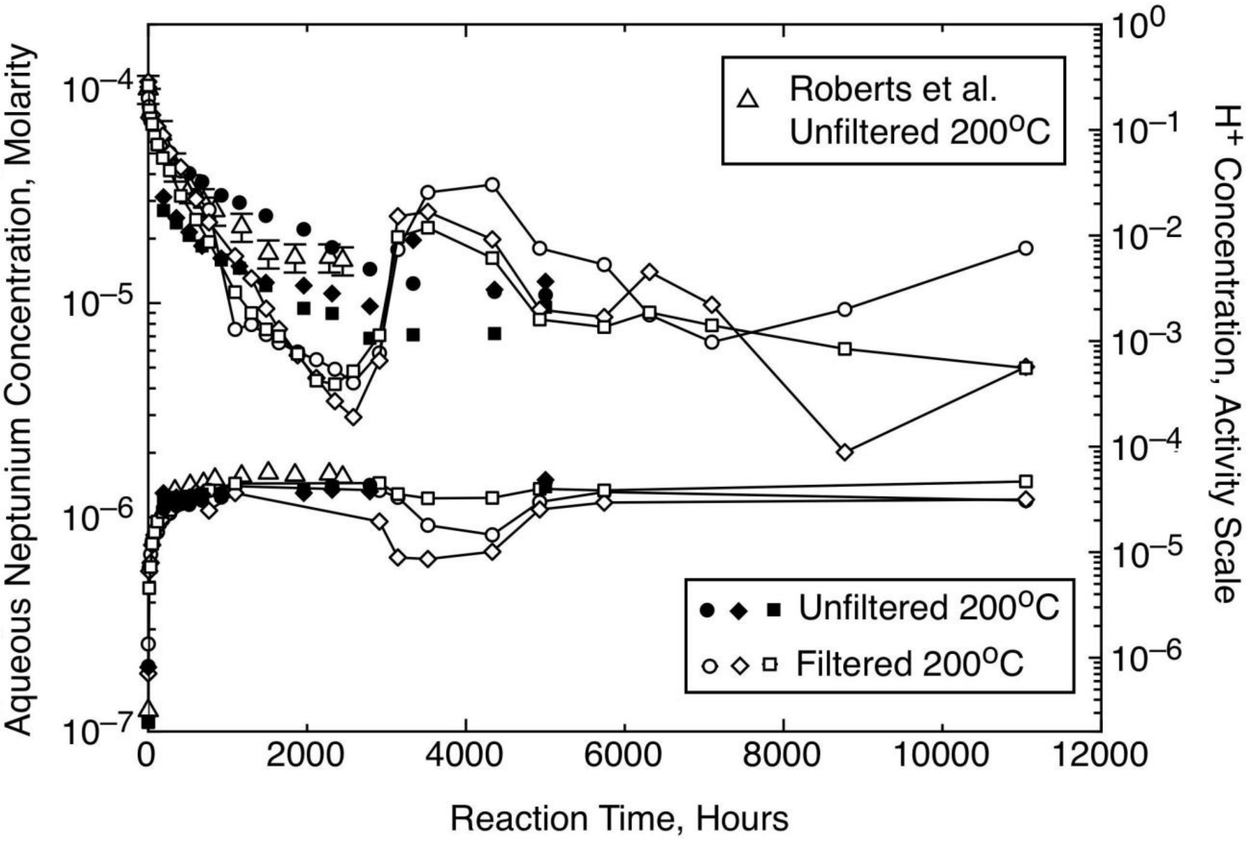

Fig. 2. Aqueous neptunium concentrations and hydrogen ion activities from NpO_2^+ precipitation experiments at 200°C using unfiltered solutions from Roberts et al. [4] and this work, and filtered solutions from this work at long times. Data in the top half of the figure use the left ordinate; data at the bottom of the figure use the right ordinate.

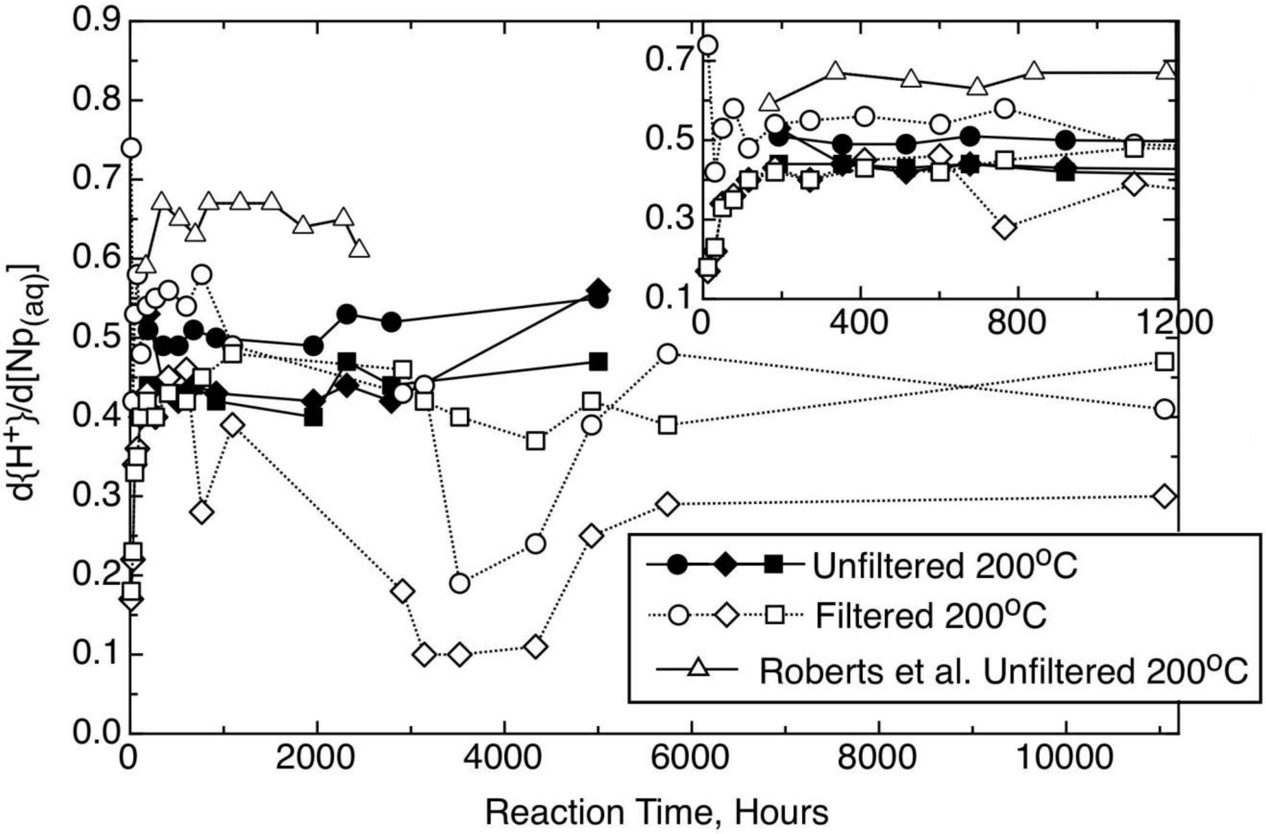

Fig. 3. d{H$^+$}/d[Np$_{(aq)}$] for unfiltered and filtered experiments at 200°C from this work and those from Roberts et al. [4]. The inset graph is an expanded view of data from 0 to 1200 hours.

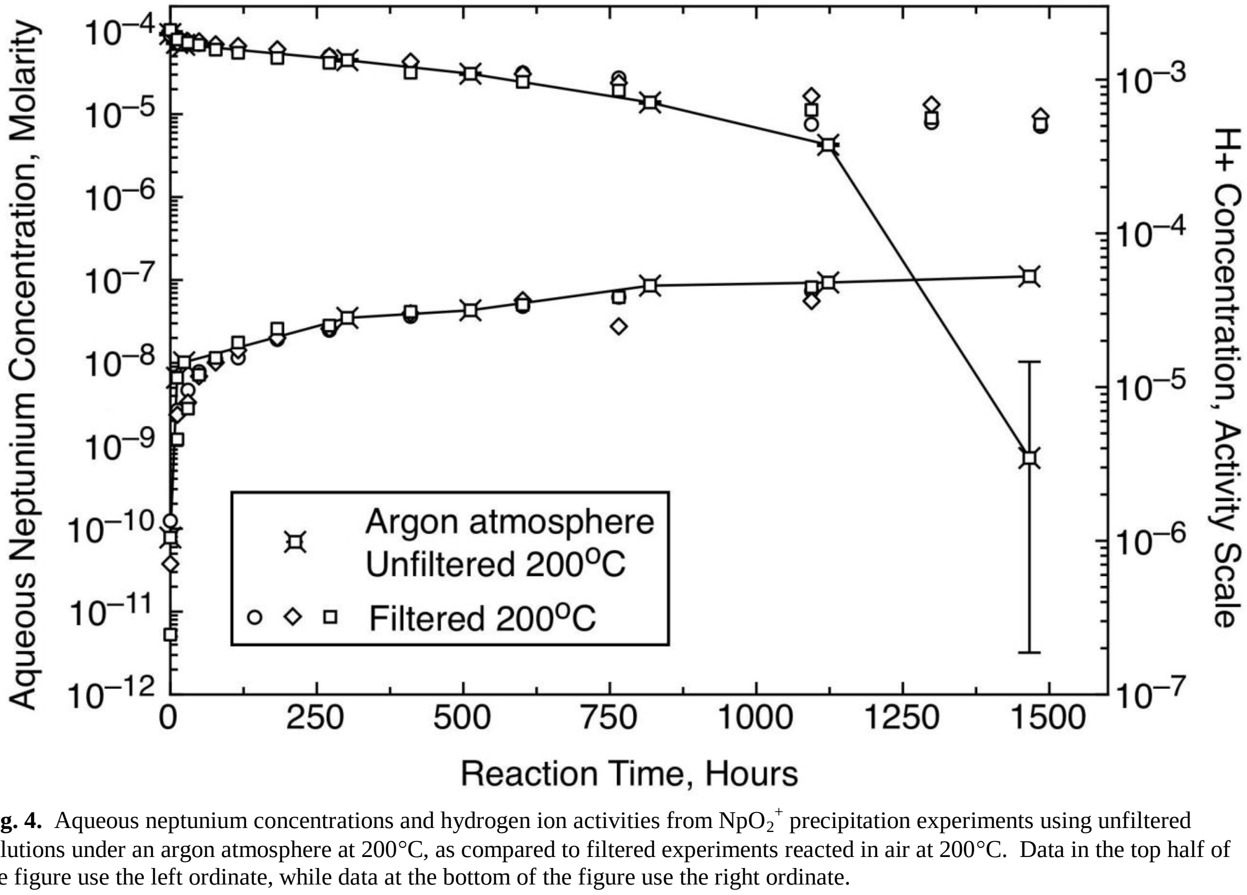

Fig. 4. Aqueous neptunium concentrations and hydrogen ion activities from NpO_2^+ precipitation experiments using unfiltered solutions under an argon atmosphere at 200°C, as compared to filtered experiments reacted in air at 200°C. Data in the top half of the figure use the left ordinate, while data at the bottom of the figure use the right ordinate.

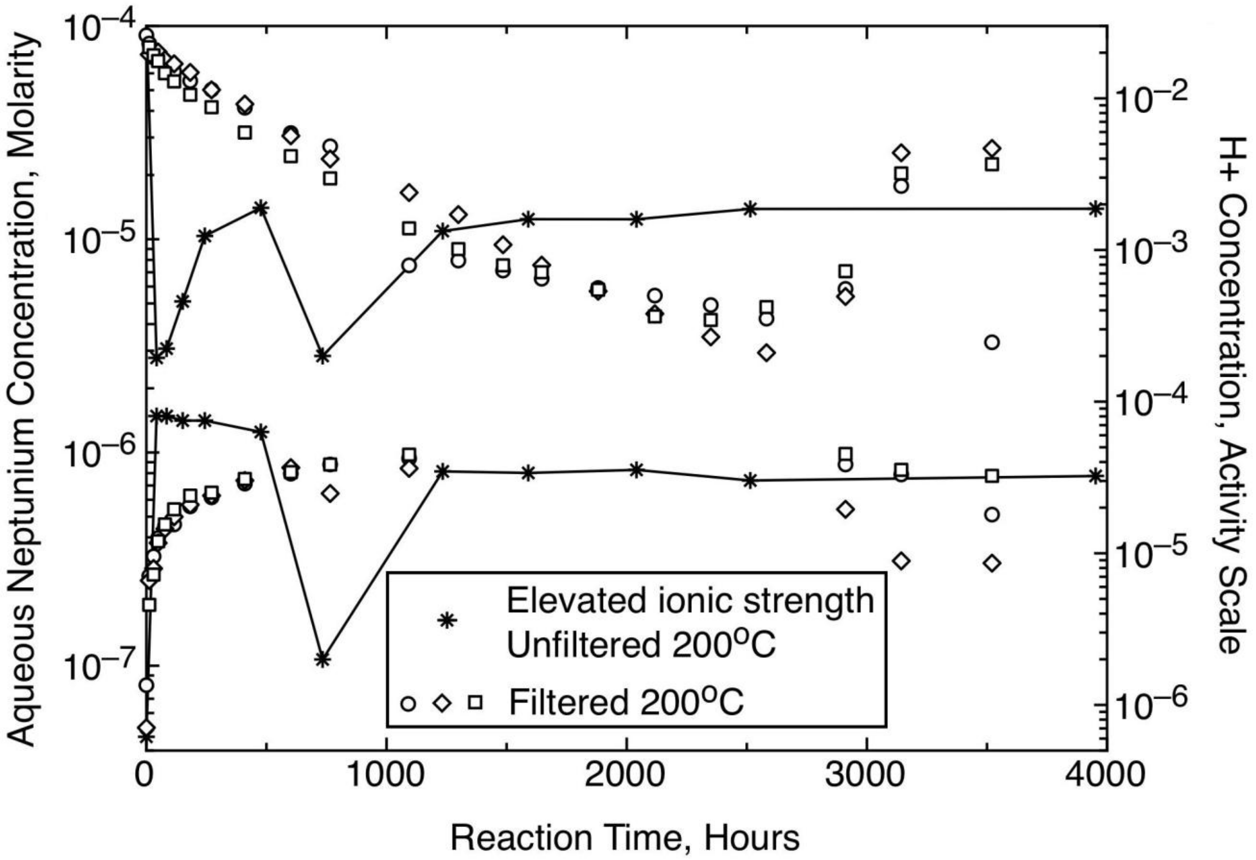

Fig. 5. Aqueous neptunium concentrations and hydrogen ion activities from NpO_2^+ precipitation experiments using unfiltered solutions in 0.05 M NaCl at 200°C, as compared to filtered experiments of very low ionic strength at 200°C. Data in the top half of the figure use the left ordinate, while data at the bottom of the figure use the right ordinate.

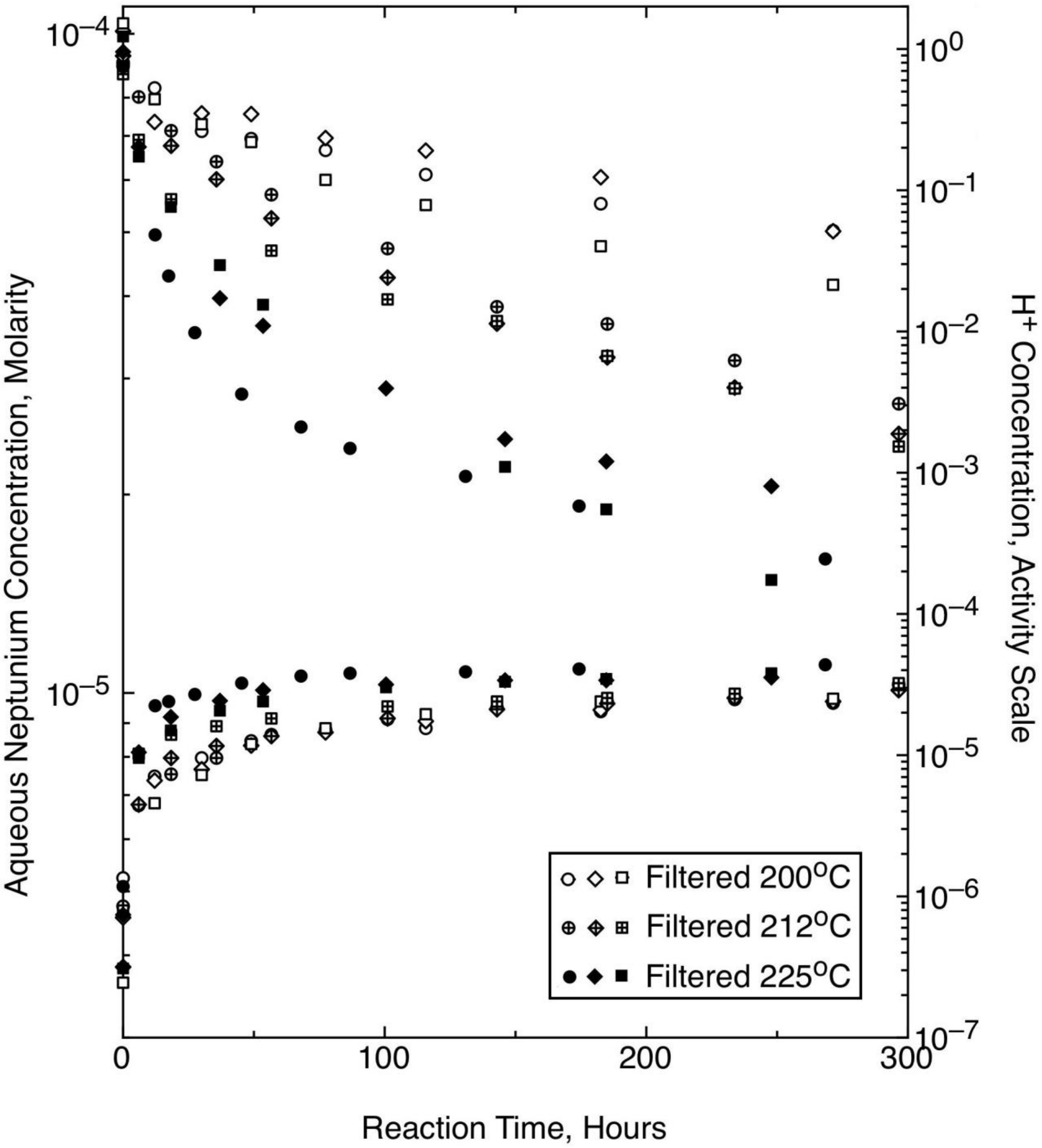

Fig. 6. Aqueous neptunium concentrations and hydrogen ion activities from NpO_2^+ precipitation experiments using filtered solutions at 200°C, 212°C, and 225°C at short times. Data in the top half of the figure use the left ordinate, while data at the bottom of the figure use the right ordinate.

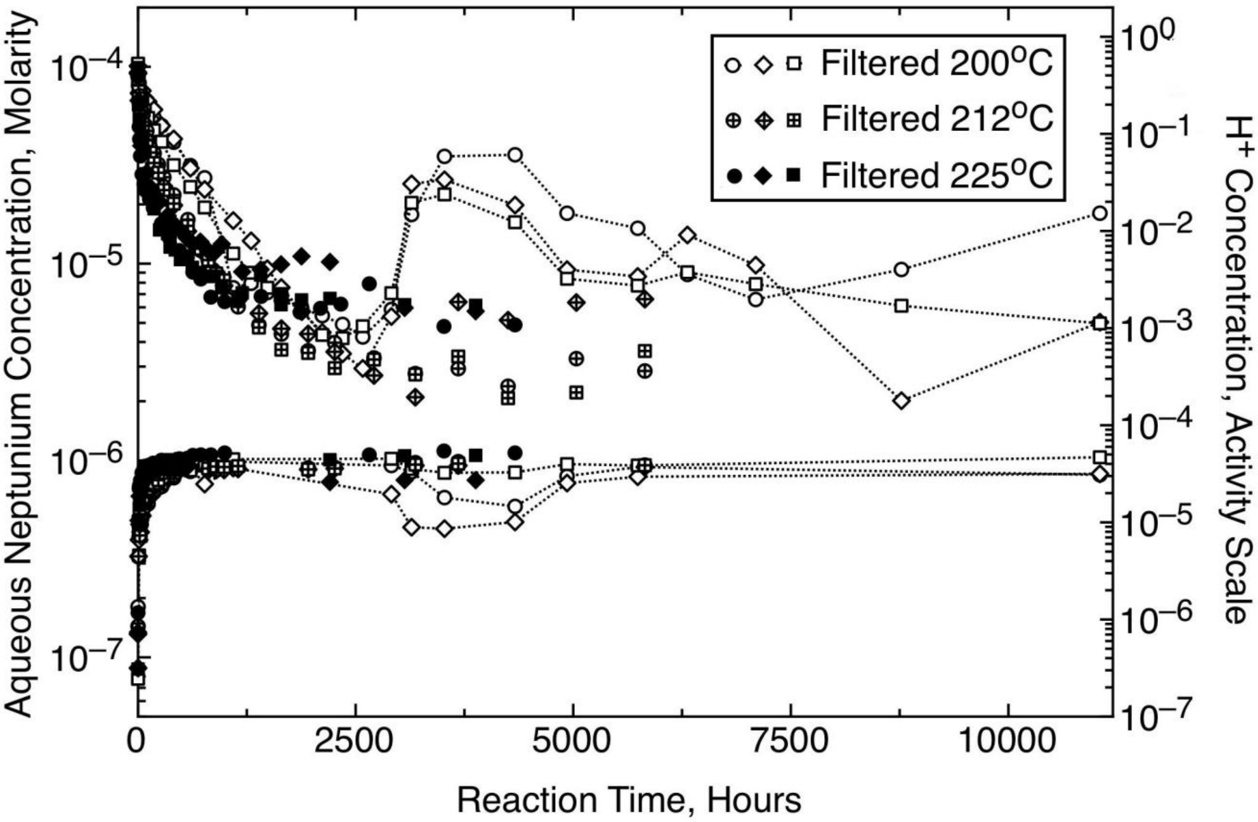

Fig. 7. Aqueous neptunium concentrations and hydrogen ion activities from NpO_2^+ precipitation experiments using filtered solutions at 200°C, 212°C, and 225°C at long times. Data in the top half of the figure use the left ordinate, while data at the bottom of the figure use the right ordinate.

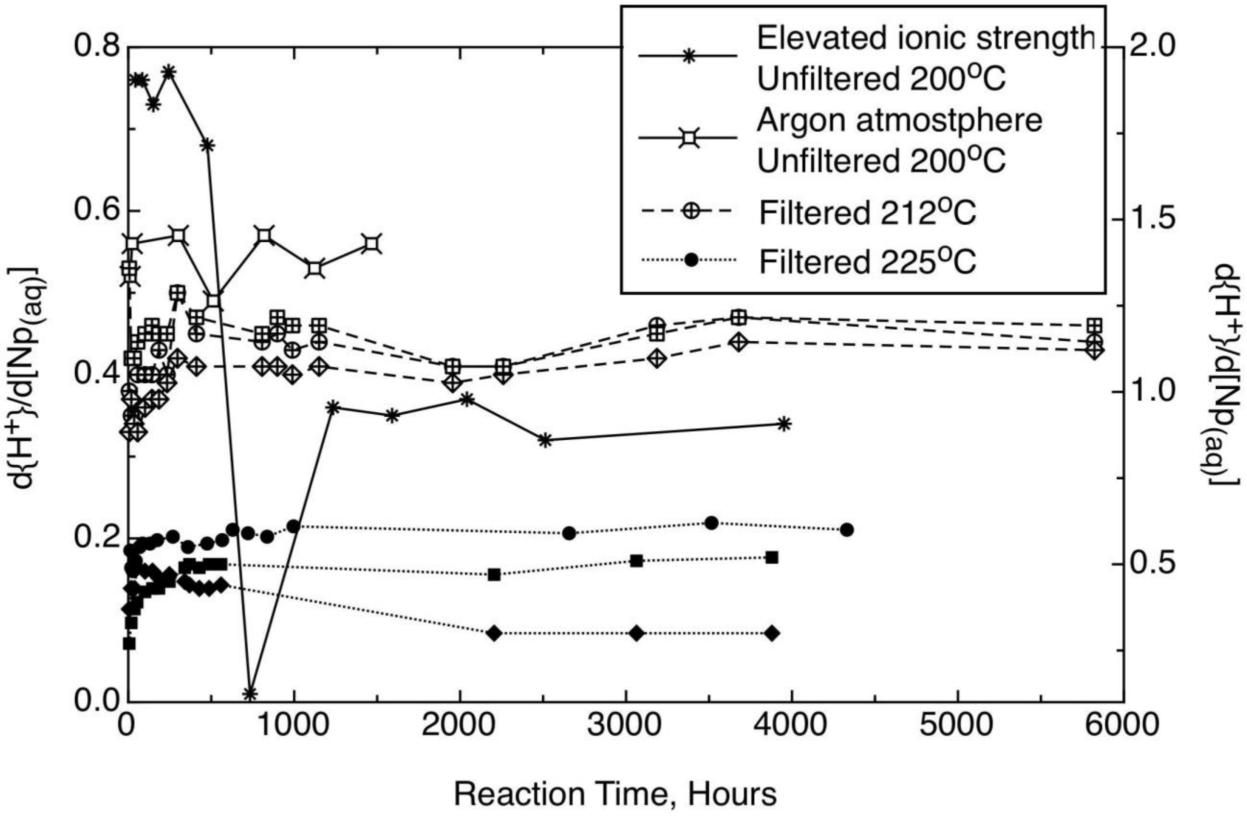

Fig. 8. d{H^{+}}/d[Np$_{(aq)}$] for unfiltered and filtered experiments at 212 and 225ºC and for unfiltered experiments at elevated ionic

strength and in an argon atmosphere. The data for filtered experiments at 225ºC (solid shapes) use the ordinate on the right; all other data use the left ordinate.

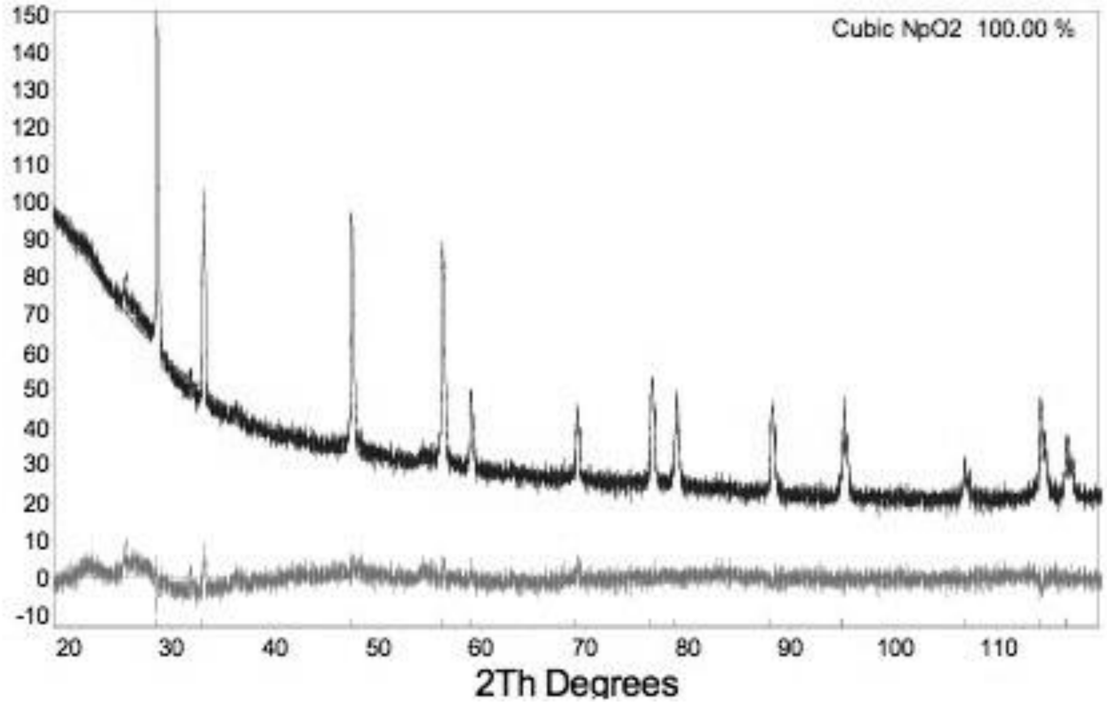

Fig. 9. X-ray diffraction spectrum measured from solids collected from a representative experiment at 225ºC (solid squares, Fig. 6 and Fig. 7).