Technical Basis for Safe Operations with Pu-239 in NMS&S Facilities (F and H Areas)

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Abstract

Plutonium-239 is now being processed in HB-Line and H-Canyon as well as FB-Line and F-Canyon. As part of the effort to upgrade the Authorization Basis for H Area facilities relative to nuclear criticality, a literature review of Pu polymer characteristics was conducted to establish a more quantitative vs. qualitative technical basis for safe operations. The results are also applicable to processing in F Area facilities.

The chemistry of Pu polymer formation, precipitation, and depolymerization is complex. Establishing limits on acid concentrations of solutions or changing the valence to Pu(III) or Pu(VI) can prevent plutonium polymer formation in tanks in the B lines and canyons. For Pu(IV) solutions of 7 g/L or less, 0.22 M HNO_3 prevents polymer formation at ambient temperature. This concentration should remain the minimum acid limit for the canyons and B lines when processing Pu-239 solutions. If the minimum acid concentration is compromised, the solution may need to be sampled and tested for the presence of polymer. If polymer is not detected, processing may proceed. If polymer is detected, adding HNO_3 to a final concentration above 4 M is the safest method for handling the solution. The solution could also be heated to speed up the depolymerization process. Heating with ≥ 4 M HNO_3 will depolymerize the solution for further processing.

Adsorption of Pu(IV) polymer onto the steel walls of canyon and B line tanks is likely to be 11 $\mu g/cm^2$, a literature value for unpolished steel. This value will be confirmed by experimental work. Tank-to-tank transfers via steam jets are not expected to produce Pu(IV) polymer unless a larger than normal dilution occurs (e.g., >3%) at acidities below 0.4 M.

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Introduction

F-Canyon and FB-Line have been processing Pu-239 for many years and have established controls for nuclear criticality safety. However, plutonium operations in H-Canyon and HB-Line prior to 1997 involved Pu-238 and Pu-242, so concerns about nuclear criticality in HB-Line and H-Canyon process and waste tanks were minimal. Processing of Pu-239 scrap from FB-Line is now in progress in H-Canyon and HB-Line. The change to processing Pu-239 in HB-Line and H-Canyon requires consideration of HB-Line and H-Canyon scenarios, which have potential for inadvertent nuclear criticality. One scenario involves Pu polymer formation and precipitation. FB-Line and F-Canyon have managed this scenario under defenses based on qualitative arguments through their Double Contingency Analyses (DCAs). The H-Canyon DCA presently has a Criticality Safety Limit (CSL) of 6 grams Pu/liter for prevention of criticality due to concentration. The corresponding limit for F-Canyon is 7 g/L Pu. In addition, the H-Canyon DCA has a CSL for solids of 45 grams of Pu-239 and a CSL for minimum nitric acid molarity of 0.5 M in any plutonium-239 storage tank. The H-Canyon minimum acid CSL prevents plutonium polymerization under normal conditions. The minimum acidity allowed in F-Canyon is 0.22 M HNO_3.

The volumes of process and waste tanks in the canyons and B lines range from 30 liters to 35,000 liters and may contain varying amounts of solution with nitric acid concentrations from below 0.01M to 14M. The process water used in H-Canyon is 0.01M nitric acid and domestic water has no added nitric acid. The process water in F-Canyon is deionized so the pH is in the range of 5 to 7. Some solutions, which must be processed through the tanks, consist of neutral or low acid scrub solutions, rainwater, and other solutions with less than 0.5 M HNO_3. Some tanks have cooling coils or jackets, which could leak cooling water into a tank. Most transfers between tanks are by steam jets, which condense steam into the solution. Limitations in equipment configuration and/or materials of construction prevent the solutions from being acidified prior to addition to some tanks containing Pu solution. Addition of any of these low acid solutions to tanks containing Pu solutions could lead to formation of Pu polymer and a potential for accumulation to unsafe levels.

A review of the literature was conducted to understand the chemistry of Pu polymer formation, precipitation, adsorption, and conditions for depolymerization in order to establish a more quantitative vs. qualitative technical basis for safe operations as part of the overall Authorization Basis upgrade for H Area facilities requested by the U. S. Department of Energy (DOE). The results of the study are given in this document.

Discussion

Chemistry of Plutonium

Basic Pu Chemistry

The chemistry of plutonium is quite complex and as such is the subject of many excellent reviews.[1,2,3] Its complexity mainly stems from its solution chemistry. In aqueous solution Pu can exist in four oxidation states (III, IV, V, and VI), readily disproportionate, undergo hydrolysis, and polymerize. The Pu oxidation states display distinct colors in solution making them easy to discern spectrophotometrically. For example, Pu(III) is blue and Pu(IV) is olive brown in an aqueous nitric acid environment. Both Pu(IV) and Pu(V) are unstable with respect to disproportionation in weakly acidic solutions. As with the other actinides (An), the tendency toward hydrolysis is dependent on charge and ionic radius, decreasing as $An^{4+} > AnO_2^{2+} \geq An^{3+} > AnO_2^{+}$. Thus Pu(VI) in PuO_2^{2+} with an effective charge of ~3.0 hydrolyzes as readily as Pu(III).

At low acid concentrations hydrolysis will produce a Pu polymer which may precipitate. This tendency to hydrolyze and polymerize explains why Pu process chemistry is mainly performed in highly acidic media.

The tendency of Pu to hydrolyze and form polymer can be illustrated with the first hydrolysis constants of Pu in its various oxidation states. The first hydrolysis constant, β_1, corresponds to the addition of an OH^- ion to an aqueous Pu ion to form a monohydroxy plutonium complex, for example,

$$Pu^{3+} + H_20 \rightarrow PuOH^{2+} + H^+ \qquad (1).$$

The monohydroxy ions formed can add additional hydroxy groups or act as a monomer to form Pu polymer. Thus, their formation can be looked at as a beginning to polymerization. In Figure 1, the percent of the total plutonium present as a monohydroxy plutonium complex for each oxidation state has been calculated using the first hydrolysis constants of Pu(III) - Pu(VI).[4] Pu(IV) complexes first appear below a pH of 2. Pu(III) and Pu(VI) complex next between a pH of 4 and 6, and Pu(V) does not complex appreciably until pH 10. This behavior follows the expected dependence on charge and ionic radius, with $Pu^{4+} > PuO_2^{2+} = Pu^{3+} > PuO_2^+$, as explained previously. The importance this trend has on Pu process chemistry, simply put, is that solutions of Pu(IV) must be kept at a higher acid concentration than those of Pu(III) in order to prevent polymerization.

The Pu oxidation states appear as distinct colors in an aqueous nitric acid environment and thus can be determined spectrophotometrically. The blue color of Pu(III) is easily discernible from the red violet or pink color of Pu(V). Pu(VI) changes color from a pinkish orange at pH 2.2 to a deep yellow at a pH of 6.3. The range of color for Pu(IV) is not nearly as great changing from a olive brown in high acid to green as the acid concentration is lowered. Absorption spectra for each of the oxidation states have been measured and are quite different.[1] The simplest spectrum as with the other actinides belongs to Pu(VI) which has a sharp peak at 833 nm. Pu(V) has two sharp peaks at 775 nm and 569 nm. The Pu(III) spectrum is the most complicated having a few broad peaks. The double peak of 560 nm and 600 nm is the most distinguishing feature. Pu(IV) has a simpler spectrum than Pu(III) with a sharp peak at 470 nm and broad peaks at 655 nm, ~815 nm, and 1100 nm.

It is interesting to note that Pu(IV) polymer has a spectrum which is different than Pu(IV). Figure 2 shows the adsorption spectrum of Pu(IV) with Pu(IV) polymer superimposed on it.[5] The main difference is that the sharp peak at 470 nm is present only as a small shoulder in the polymer spectrum, which has a very high absorbance below 450 nm. Additionally, the broad peaks of the Pu(IV) spectrum have decreased in intensity and broadened further. The unique spectra coupled with the fact that Pu(IV) polymer obeys Beer's Law has been used extensively in the literature to quantify Pu(IV) polymer.[6,7,8,9,10] The wavelength used is usually between 400 nm and 600 nm, for example, Brunstad[7] used 415 nm.

The important Pu chemistry of the aqueous nitric acid system used by H-Canyon and HB-Line is that of Pu(IV). While both Pu(III) and Pu(IV) exist in this environment, Pu(III) is oxidized with HNO_2 to take advantage of the greater extractability of the more highly charged Pu(IV). Pu(IV) will disproportionate by the reaction,

$$3Pu^{4+} + 2H_2O \rightarrow 2Pu^{3+} + PuO_2^{2+} + 4H^+ \qquad (2)$$

if the HNO_3 concentration is less than 1M. Here it should be noted that the rate of disproportionation is far slower due to the formation of the Pu-O chemical bonds than the oxidation rate of Pu(III) to Pu(IV), which is by electron transfer. Thus, the disproportionation effects can generally be neglected if the H^+ concentration is high or if a holding oxidizer is present. Pu(IV) is the dominant species in solution at $pH < 1$.

The important Pu chemistry of the aqueous nitric acid system used by FB-Line and F-Canyon is that of Pu(III) and Pu(IV) respectively. F-Canyon, uses Pu(IV) for solvent extraction. FB-Line uses higher concentrations of Pu and a reductant is added to keep Pu as Pu(III). As noted above, Pu(III) forms polymer at a much lower acid concentration than Pu(IV). Pu(III) polymerizes probably as $Pu(OH)_3 \bullet xH_2O$, a blue or pale purple gelatinous precipitate, which immediately turns green due to oxidation to Pu(IV) hydroxide. However, this polymerization is highly unlikely in the F Area processes because the acid concentration in the vessels is maintained above 0.22 M HNO_3 in case the reductant is lost and Pu(IV) forms. Hydrolysis of Pu(III) is thus not as important an issue as is the hydrolysis of Pu(IV).

The hydrolysis of Pu(IV) initially forms Pu hydroxides between a pH of 1-1.5. The reaction can be written as:

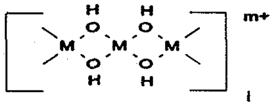
$$Pu^{4+} + iH_2O \Leftrightarrow Pu(OH)_i^{(4-i)} + iH^+ \qquad (3)$$

which shows that the solution acidity increases with hydrolysis. The formation constants, β_i, for Pu(IV) hydrolysis as defined by:

$$\beta_i = [Pu(OH)_i]^{4-i}/[OH^-]^i[Pu^{4+}] \qquad (4)$$

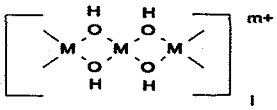
are large ($\log \beta_1$=12.2, $\log \beta_2$=24.6, etc.)[6,11] and increase considerably with each additional OH^-. Thus, the equilibrium is to the right and produces a mixture of hydrolysis products above pH 1.5. The hydrolysis products may then undergo polymerization through the formation of hydroxy bridges.[12]

$x\text{-}M(OH)_i^{(4-i)+} - y.H_2O \rightarrow$

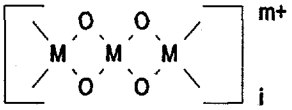


(5)

Aging or further dehydration by transformation of the hydroxy bridges to oxo bridges follows.



$- y.H_2O \rightarrow$



or $[MOMO]_i^{m+}$ (6)

Such polymerization, depending on the concentration of Pu, hydrogen ion, temperature, and time will produce colloids, sols, and/or polymer precipitates.

The aggregation and aging steps above explain the divergent properties of Pu(IV) polymer. For example, Pu(IV) hydroxide, a dark green material which becomes black upon drying, can be prepared by precipitating Pu(IV) with excess NaOH, KOH, or NH_4OH. It can be represented by $Pu(OH)_4$ or possibly $PuO_2 \bullet aq$. In contrast, Pu (IV) polymer is a bright emerald green material, which has different properties depending on how it is made. The polymer can be made by dissolving $Pu(OH)_4$ with less than 4 moles of H^+ ion per mole Pu suggesting an aggregation step. The polymer once formed is hard to dissolve and becomes even more so after aging. Diffraction patterns of the polymer exhibit an increasingly crystalline structure, corresponding to a cubic PuO_2 fluorite, as the polymer is aged.[13] Recent EXAFS (Extended X-Ray Absorption Fine Structure) studies point to a similar structure.[14]

The aggregation and aging steps can explain the variable size and colloidal properties of the polymer as described in the literature.[15,16] Colloidal size is due to two competing processes: the formation of new nuclei and the growth of aggregates. A slow rate of formation of new nuclei and a rapid aggregation lead to a small number of large particles. Such particles would take longer to dissolve and are more likely to precipitate. On the other hand, a high formation rate for new nuclei and a slow rate of aggregate growth forms a large number of small particles, which would dissolve more quickly, but may stay suspended in solution. Additional aging would produce a harder to dissolve and easier to precipitate polymer due to increased crystallinity as the oxo bridges form. The above statements agree well with the experimental data, which show the importance of method of preparation on the resulting properties of the polymer.

The diverse properties of Pu(IV) polymer must be taken into account when doing Pu(IV) process chemistry. Obviously, polymer properties such as adsorption and precipitation must be understood especially in cases with criticality issues, where adsorption and precipitation are to be avoided. To avoid polymerization the following questions need to be answered. Under what conditions, temperature, concentration of acid, or concentration of Pu, is polymer made? If polymer is accidentally made will it stay suspended in solution, how should it be dissolved and what should it be dissolved with? An attempt will be made to answer these questions for the conditions important for running HB-Line, H-Canyon, FB-Line, and F-Canyon.

Polymerization

Pu(IV) polymer can be prepared in many different ways, each of which imparts specific properties to the polymer. A few general methods are: 1) treating Pu(IV) hydroxide with less than 4 moles of H^+ ion per mole Pu, 2) adjusting the H^+ ion concentration of a Pu(IV) nitrate solution to about 0.1 M and letting the solution stand or be heated, 3) dribbling a concentrated solution of Pu(IV) into boiling H_2O, and 4) extracting HNO_3 from an HNO_3-$Pu(NO_3)_4$ solution by means of a long chain amine or alcohol. All of these methods produce "fresh" polymer initially. The polymer becomes "aged" by letting it stand for more than a few days or by prolonged heating. The final method produces sols, which can be stable in solution for months.

Pu(IV) polymerizes to a greater extent if temperature or Pu concentration is increased or total acidity is decreased. Brunstad[7] quantified this very early by finding that polymerization occurs in solutions less than 0.3 M H^+ at room temperature (25°C) and less than 1.23 M H^+ at boiling (100°C). He also found that, in the 1 g/L -15 g/L Pu solution range, polymerization begins at higher acidity and is more extensive at the higher Pu concentrations. Costanzo, et al.,[8,17-19] using 2.1 g/L Pu at 25°C found similar trends. No polymer formed when the initial acidity was 0.1 M, but the degree of polymerization continuously increased as the acidity was lowered and was almost quantitative at 0.04 M. More recent systematic studies,[20] most notably by Miles[21] at higher Pu concentrations, confirm these trends.

Pu(IV) polymerization can be effectively decreased by the addition of $UO_2(NO_3)_2$ or citric acid. Toth, et al.,[9] found that 0.05 M - 0.5 M $UO_2(NO_3)_2$ added to 0.5 M Pu(IV) at 50°C lowers the production of polymer by ~35%. Additions of 1 M $NaNO_3$ or 0.5 M $Ca(NO_3)_2$ did not react similarly, ruling out a common ion effect of NO_3^- or an ionic strength effect in the solution. The uranyl ion, UO_2^{2+}, must act as a chain termination step by attaching to the hydroxyl groups on Pu(IV) preventing further aggregation. Alternatively, a Pu-U complex much like the strongly complexed di-uranate species $(UO_2)_2(OH)_2(NO_3)_2{\bullet}4H_2O$ may be formed. Citrate which complexes strongly to Pu has been shown to decrease polymerization.[22] One would expect other strong chelators such as EDTA to behave similarly.[1] Surprisingly, F^- which is known to help dissolve Pu polymer does not prevent its formation at low acidities.[8] For a solution initially 2.2 g/L in Pu, 0.4 M HNO_3, 0.02 M $Al(NO_3)_2^-$, and 0.05 M NaF the extent of Pu(IV) polymerization was found to be comparable to a similar solution not containing F^-.

Precipitation

Addition of anions or moderately concentrated acid will precipitate the polymer if it is present in solution. In the initial work on Pu by Kraus[10], it was found that 0.15 equivalents of IO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{2-}, or $Fe(CN)_6^{2-}$ per mole Pu present as polymer, are sufficient for essentially complete precipitation of the polymer. Additionally, the polymer could be precipitated in moderately concentrated nitric acid without depolymerization. The polymer could be re-dissolved with further excess acid. Bell et al.,[19] determined that fresh polymer would not precipitate when nitric acid was added and that aged polymer would precipitate between ~0.5 M and 4.0 M acid. More importantly, precipitation was found to be controlled by the NO_3^- concentration. Over the same nitrate concentration region the percent polymerization was found to be the same for HNO_3, $Al(NO_3)_3$ and $NaNO_3$ suggesting a common ion effect. $LiNO_3$ was an exception, however, producing considerably more precipitation over a greater NO_3^- concentration range. From these studies, it is apparent that in most Pu processing, in order to keep the polymer from precipitating, the total nitrate ion concentration should be above 4.0 M and addition of $LiNO_3$ should be avoided.

Partial neutralization of acidic Pu(IV) solutions can result in the formation of colloidal suspensions that are highly stable and behave like solutions in many respects. These highly stable colloidal solutions of Pu polymer, called sols, are ideally stabilized at NO_3^- to Pu mole ratios between 0.8 and 1.0.[13] Sols may be stable regardless of the amorphous or crystalline characteristics of the primary polymeric particles. Sols will not exist at the process concentrations used in F or H Area and will not be discussed further.

Smaller concentrations of Pu(IV) polymer may also be stable in solution. For example, 5×10^{-4} M (0.1 g/L) Pu is stable as a suspension for six months at a pH of 2.0. Concentrations of Pu(IV) polymer this low are generally far below process concentrations and are studied for environmental purposes. Above pH 5 these polymer suspensions are not stable and they settle out in less than six days.[23]

Precipitation Rate

The precipitation rate of Pu(IV) polymer varies considerably. Pu(IV) precipitates as $Pu(OH)_4$ immediately in strong base. Peptization of this hydroxide produces polymer that can be suspended in solution almost indefinitely as a sol. The suspension time depends on the polymer's colloidal properties of charge and size. The complete precipitation of the polymer mentioned earlier with 0.15 equivalents of IO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{2-}, or $Fe(CN)_6^{2-}$ per mole Pu, can be explained by a neutralization of the polymer charge. Precipitation due to charge neutralization occurs rapidly with colloids and can be said to be immediate. A similar rate is expected for the addition of HNO_3 to a solution of aged polymer, which causes charge neutralization between 1.0 M and 4.0 M HNO_3. Polymer suspended in solution also precipitates due to its size. Large polymer precipitates more quickly than small polymer. For example, an hour centrifuging at 5000 rpm precipitates 35.9% of aged polymer but only 6.2% of fresh polymer.[15] The difference in percent precipitation is apparent even after 70 hrs at 6500 rpm. The only rate study on Pu polymer precipitation is by Rai and Swanson.[23] Using an aged solution of 0.1 g/L Pu, they found that polymer stayed suspended for 6 days at pH 3.8, but precipitated almost quantitatively above pH 5.0. They also determined that the polymer solubility above pH 3 is between that of $Pu(OH)_4$ and $PuO_{2(c)}$ and it drops ~0.75 log units with each unit increase in pH.

Polymerization Rate

The rate of polymer formation has been found to be quite complicated. The rate has been reported as immediate in the case of adding water to concentrated Pu solutions to days in other preparations. In general, all researchers have found that the rate increases with increasing Pu concentration, decreasing acid concentration, and increasing temperature.[17-19,21,24] Toth and Osborn[24] even found that Pu polymer formation occurred upon reflux in 6.0M nitric acid where it did not at room temperature. The importance of acid concentration on the rate can be seen in Figure 3. Note that a change in acid concentration from 0.1 M to 0.04 M in a 2.1 g/L Pu(IV) solution effectively changes both the rate and extent of polymer formation drastically.

Empirical models for the stability of a Pu solution with respect to formation of polymer have been developed. The empirical model developed by Toth and Dodson[24] predicts the time it takes to convert 2% of the Pu(IV)in solution to polymer at a given temperature. The percentage used is twice the detection limit of the spectrophotometric system that was used to gather the data to form the basis for the model expressed as:

$$t = [Pu_T]^{-1.6}\,[HNO_3]^{4.6}\,(7.66 \times 10^{-16})e^{12,300/T} \qquad (7)$$

where t is in hours, $[Pu_T]$ and $[HNO_3]$ are molar concentrations of the total plutonium and nitric acid, and T is temperature in Kelvin. A more restrictive model to estimate the approximate limiting Pu(IV) concentration at 25°C over a range of 1-100 g/L Pu is given by the equation:[26]

$$[Pu(IV)] = 9000[HNO_3]^4 \qquad (8)$$

where [Pu(IV)] is in g/L and $[HNO_3]$ is in molarity.

Figure 4 shows the stability lines obtained with the empirical models for the Pu nitric acid system. The solid lines are the stability lines predicted by the Toth and Dodson[25] equation for Pu(IV) solutions between room temperature and boiling. The time needed to produce 2% polymer was chosen as 4 days in order to compare it to the earlier data of Brunstad[7] and as a conservative time a solution would stay in a tank prior to being moved. The dashed line is the more restricted model. A Pu(IV) solution will be stable to the right of the stability line and to the left it will polymerize. Using present H-Canyon limits of 0.5M acid and 6.0 g/L Pu as an example, the solution will polymerize 2% in four days if the solution temperature is above 75°C. It is important to realize that the stability lines are for producing Pu(IV) polymer. Lowering the acid concentration in a 1 g/L Pu solution from 1 M to 0.1 M at 50°C will produce polymer, but once produced raising the acid from 0.1M to 1M will precipitate the polymer, before slowly dissolving it. At the higher concentration of 50 g/L Pu, the solution will polymerize the same amount above 25°C.

For process chemistry, it may be important to use the empirical model developed by Toth and Dodson[25] to predict the time it takes to convert 2% of the Pu(IV) in solution to polymer at a given temperature. Two attempts have been made to predict the time of polymerization. These are shown in Figures 5 and 6. In Figure 5, the time it takes a 2 g/L Pu(IV) solution to polymerize 2% of the Pu at various HNO_3 concentrations and temperatures is shown. The line drawn at 12 hrs (one shift) once again points out that at higher temperatures more acid is needed to keep from forming polymer. At acid concentrations below 0.1 M, the time it takes to polymerize is far shorter than a shift. Similarly, at higher Pu concentrations more acid is needed to keep from polymerizing, which can be seen from Figure 6. Here the time it takes to polymerize at 35°C is shown. The times chosen are based on F and H Area process chemistry, i.e., the filling of a large tank (2 hrs), a shift (12 hrs), two shifts (1 day), a few days, and a week. A very small change in acid concentration makes a large difference in polymerization time suggesting that a slight excess of acid above any of the polymerization lines in Figures 4, 5, and 6 would be advantageous.

Depolymerization

Pu(IV) polymer can be depolymerized by strong acid addition, and oxidation or reduction. Depolymerization with 1-2 M HCl or HNO_3 is essentially negligible but becomes appreciable in 6-10 M HNO_3. Fresh polymer can be dissolved with less than 4.0 M HNO_3. In practice, low acid dissolution is avoided in process chemistry because of the possibility of the polymer produced being aged polymer, which may precipitate before it dissolves. Treating aged polymer with boiling acid > 4 M HNO_3 will in time destroy it. The addition of strongly complexing anions, such as SO_4^{2-} or F^-, to HNO_3 will increase the depolymerization rate substantially.[8] Reduction to Pu(III) with hydroxyl amine or oxidation to Pu(VI) with permanganate, dichromate ($Na_2Cr_2O_7$),[27] or Ce(IV)[28] will also destroy the polymer.

Depolymerization Rate

Fresh and aged polymers have been found to depolymerize at different rates. Depolymerization of fresh polymer proceeds as a first order reaction in Pu polymer concentration. As noted earlier, fresh polymer does not precipitate with the addition of between 0.5 M – 4.0 M HNO_3 while aged polymer will. Depolymerization of aged polymer is slower than fresh polymer and even more so if it was formed at higher temperatures. In attempting to quantify depolymerization, Biggers and Costanzo[8] determined half times or the time for half of an amount of polymer to depolymerize under various conditions. Half times for unaged polymer and polymer aged for 24 hrs were 7 hours and 100 hours, respectively, when using 1 M HNO_3. Aged polymer was more easily depolymerized with the addition of strongly complexing anions, such as SO_4^{2-}, or F^-. In fact, using 5.0 M HNO_3 with 0.05 M F^- produced complete depolymerization in less than 5 minutes. Addition of 0.20 M $Al(NO_3)_3$ to the F^- solution slowed depolymerization by a factor of 5 but its addition was suggested in order to lower corrosion of process equipment.

The important points of Pu(IV) depolymerization are illustrated by a plot of depolymerization half times as a function of acid concentration in Figure 7. Two groups of points are evident in the figure, those of aged polymer which take a long time to depolymerize and those of fresh polymer which depolymerize much faster. The two points above 350 hours are precipitates. Aged polymer below 4.0 M acid is seen to depolymerize at a very slow rate. However, the rate is much faster when 6.0 M acid is used. At 5.0 M acid, the vastly different half times of aged polymer are due to the method of preparation. The 200 hour half time polymer was aged at room temperature "for a long time"[29] before use while the 320 hour half time was aged by boiling for 24 hours. The final aged point of Kraus[27] appears to have been aged by letting it stand at room temperature for a few days. The points for fresh polymer appear to be broken into two groups[7,8,29] which intersect at ~5.5 M HNO_3. The lower group is expected for fresh polymer in that it depolymerizes quickly with half times ranging from 20.1 hours to 1.2 hours in 1.0 M to 10 M acid.[8] The other group of fresh polymer data does show longer depolymerization times between 1.0 M - 4.0 M acid akin to aged polymer.[7,29] The difference between the two groups of data is that the first group was centrifuged and only the polymer left in solution was used in the depolymerization experiments. The second group was not centrifuged and presumably would have a higher content of more crystalline polymer, which would take a longer time to depolymerize. The non-centrifuged fresh polymer is more representative of polymer produced in a process environment, which would explain why depolymerization procedures call for greater than 4.0 M and preferably 6.0 M acid to be used.

The rate of oxidative depolymerization was examined by Savage and Kyffin[28] with Ce(IV) in 0.03 M – 3.0 M HNO_3. Addition of ceric ammonium nitrate to 0.14 g/L Pu polymer in dilute nitric acid at 16.1°C resulted in depolymerization half times in the 5-30 minute range for polymer aged 4 hours to 4 months. This is the same amount of time seen in depolymerization with F^- at higher acid concentrations. Oxidation of 0.14 g/L Pu polymer by Ce(IV) was fastest when 0.005 M Ce(IV) was used in 0.3 M HNO_3. The depolymerization rate was found to increase with Ce(IV) concentration between 0.002 M - 0.1 M, and with Pu concentration between 0.23 mg/L - 0.23 g/L. The rate increased with acid concentration from 0.03 M to 0.3 M and then decreased to 3.0 M. A suggested mechanism involving $[Ce_2O(OH)_2]^{4+}$ as an intermediate explains the acid behavior of the Pu depolymerization.

Adsorption

When plutonium polymer forms in solution, it may adsorb onto the walls of tanks, piping, etc. Ockenden and Welch[29] observed adsorption of Pu(IV) polymer onto polished steel of 4 $\mu g/cm^2$. For unpolished steel, their value was 11 $\mu g/cm^2$. Glass exhibited a much lower value, 1.6 $\mu g/cm^2$. It is important to note that these values are for plutonium, which remained after the surfaces were "washed well with 0.1M nitric acid". In their experiments, Ockenden and Welch used plutonium (IV) concentrations of 1-3 g/L, and immersed the materials in colloidal Pu(IV) solution for 7 days. No other numerical values for Pu adsorption onto stainless steel were found.

A quick calculation provides an estimate of plutonium adsorbed onto tank walls and surfaces. Consider a solution of 14,000 L in an 8-ft diameter tank. The top of the solution would be 10 feet high. This corresponds to a surface area of:

$$\pi r^2 + 2\pi rL = 16\pi + 80\pi = 302 \text{ ft}^2 \qquad (9)$$

The tank coil is made of roughly 494 linear feet of 2" schedule 80 pipe, yielding 307 ft^2 of surface area. The sum, 609 ft^2, is increased by 10% to account for the agitator, dip legs, and anti-swirl baffles. This gives a total exposed surface area of 670 ft^2. Using the literature values for adsorption, 2.5 g of plutonium would remain on the exposed surfaces if they correspond to polished steel. If the surfaces correspond to unpolished steel, 6.8 g of plutonium would be adsorbed. As mentioned previously, the adsorption value used for these calculations is for aged (7 days) plutonium polymer that would remain after rinsing with 0.1M HNO_3. The adsorption for short residence times and the amount of plutonium remaining on a wet tank wall are not known. In addition, the difference in adsorption between polished and unpolished steel suggests the need to conduct experiments using steel as similar as possible to that found in H-Canyon tanks.

Other studies found in the literature give us a better understanding of the adsorption/desorption behavior of Pu(IV) polymer. Samartseva[30,31] observed Pu adsorption on polished platinum as well as on glass and polished quartz. For platinum, the maximum adsorption occurred when the pH was between 1.5 and 3 with HNO_3. For quartz and glass, the maximum occurred for pH values of 3 to 4. Interestingly, Samartseva observed that quartz disks immersed for two hours, removed from solution and kept in air for 10 minutes, then re-immersed in the same solution for two hours, yielded 1.5 times more adsorption than disks immersed continuously for 4 hours. This observation suggests the need for similar tests on stainless steel. If similar behavior occurs on steel, solutions containing Pu(IV) polymer could deposit some polymer on tank walls, and subsequent solutions could deposit more polymer. It should be noted that Samartseva was working with quartz disks in solutions having Pu concentrations of 1×10^{-8} M or lower. Whether such behavior occurs on stainless steel and at higher Pu concentrations needs to be examined in the laboratory.

In earlier work, King[32] studied Pu(IV) adsorption on glass at a plutonium concentration of 10^{-9} M. Pu adsorption increased with decreasing acidity, and at a nitric acid concentration of 0.0006 M (pH=3.2), plutonium adsorption on glass reached 50%. In other words, the amount adsorbed was equivalent to the amount not adsorbed. King's experiments, however, were performed with very small pipettes, which gave a high surface area to volume ratio that is not found in large tanks. King did show that rinsing glass with water was not effective in removing adsorbed plutonium. Rinsing twice with water did not remove as much adsorbed plutonium as a subsequent rinse with warm (70°C) 1 M HNO_3.

Other reported data on adsorption of Pu(IV) polymer on different surfaces sometimes conflict. Samartseva found that adsorption decreases in the order Pt > quartz > glass. Haissinsky, et al.[33,34] found that for solutions approaching 1 g Pu/L, adsorption decreased as: stainless steel > PVC > Pt; their kinetic study at low Pu, however, showed Pt adsorbing more than stainless steel. This stainless steel had been electrolytically polished in acid solution, and previous work[29] has shown that polished steel adsorbs less Pu than unpolished steel. Garnett and Whittaker[35] used a plant process solution and found polyethylene > PTFE > Perspex > Ta > PTFCE > stainless steel > Ti > Pyrex. In light of this latter work, using PTFE (Teflon) or PTFE-coated containers during experimental work is ill-advised.

Desorption

To remove adsorbed Pu(IV) polymer for quantitative analysis, Ockenden and Welch[29] first washed specimens with 0.1 M nitric acid, then removed the polymer using hot 5 M nitric acid. They do not indicate how much Pu was removed by the initial wash. King [32] found that washing a thin glass pipette with water removed some of the remaining plutonium. King defined a wash as simply letting the wash solution stand in the pipette for 2.5-3.5 minutes, then draining it. After two washes with water, however, a wash with warm (70°C) HNO_3 removed more plutonium than the combined water washes. King attributed this to desorption by warm nitric acid. King followed with another wash using either warm nitric acid or 36 N sulfuric acid, and found that very little plutonium remained after the first warm nitric acid wash.

As an alternative to desorption, Pu (IV) polymer can be destroyed by oxidation to Pu(VI) (i.e., $Na_2Cr_2O_7$ or Ce(IV)) or reduction to Pu(III) (i.e., hydroxylamine) or by the addition of a complexing agent (i.e., SO_4^{-2}, F^-) in acidic media.[27] Costanzo and Biggers,[8] for example, found that SO_4^{-2} and F^- increased the rate of depolymerization in 5 M HNO_3.

In summary, adsorption of plutonium polymer onto tank walls is a concern that requires experimental work for further quantification. Literature values for adsorption onto unpolished steel indicate that 6.8 g of Pu(IV) polymer could deposit in a given tank from a 14,000 liter batch of Pu solution. There is experimental evidence to indicate that more Pu can be adsorbed from subsequent batches. Note that Pu adsorbed on surfaces inside a tank does not represent a geometry used in criticality calculations. There is no data to indicate how thick a layer of Pu can be adsorbed or if thicker layers would begin to flake off the walls.

Safe Operation

The information in this section is intended for use in tanks where the geometry is not controlled. Tanks with favorable geometry do not require controls because polymer formation and possible precipitation on aging does not result in nuclear criticality safety concerns. The literature reviewed above provides most of the information needed to define safe operating areas, which either avoid Pu polymer formation or prevent precipitation of polymer. The conditions, which can lead to polymer formation, involve solutions with low acid concentration. One thing is clear from the literature on Pu polymer formation; although polymer formation can occur without precipitation, immediate precipitation is possible if water is added[7] to concentrated Pu solutions or if electrolytes especially lithium nitrate, or the anions, sulfate, phosphate, and oxalate[19] are added to aged polymer. The latter three ions are often found in process or waste solutions. Under most process conditions, Pu polymer forms as colloidal size particles with residual surface charge and remains suspended in solution. The polymer can come out of solution in one of three different ways: adsorption on surfaces inside the tank, crystallization, or agglomeration into particles large enough to precipitate. The first two ways are predominant in the literature reports. Even transient low acid concentrations can lead to formation of polymers, which will depolymerize if the acid concentration is high enough after complete mixing of the solution.

Formation of polymer is dependent on the acid concentration, temperature, and Pu concentration as shown in Figure 4. Crystallization or aging of Pu polymer in solution is a kinetic process, and as a result, can vary in time depending on the temperature and acid concentration. If the acid concentration is high enough, the rate of dissolution can be equal to or faster than the rate of crystallization and the polymer dissolves or depolymerizes before any precipitation can occur. Figure 7 shows the time to depolymerize fresh and aged polymer. The rate of depolymerization is also temperature dependent so that both rates are faster at higher temperature. Short depolymerization times are assured only at acid concentrations ≥ 4 M. Although Brunstad recommended that Pu solutions never be diluted with water, the rapid depolymerization of fresh polymer above 4 M HNO_3 shows that high acid solutions can be diluted with water safely as long as the final acid concentration is above 4 M.[7] Later studies suggested diluting Pu solutions with 0.1 M HNO_3.

Another method for avoiding Pu polymer is changing the valence state of Pu. Pu(III) and Pu(VI) polymerize at much higher pH than Pu(IV) (see Figure 1); so adjusting the Pu valence to Pu(III) prior to addition of water or low concentration acid would avoid polymer formation. Solutions containing U are also less likely to form Pu polymer. Polymer can form in the dissolver, if the solution is allowed to go "acid deficient". Dissolver solutions in F-Canyon which contain >250 g/L U with < 1 g/L Pu will not form polymer on addition of neutral solutions such as gelatin as long as the acid concentration after addition is above the minimum provided in the DCA. It is preferable to have the acid concentration above 0.5 M when gelatin is added. Uranium acts to cap the polymer chain at very small numbers typically preferring dimers or trimers rather than longer chain polymers.[9] The dimers and trimers are soluble.

Adsorption onto tank surfaces, agitator, and cooling coils gives very thin layers of polymer very strongly adhered to the surface. The polymer crystallizes to $PuO_2 \bullet 2H_2O$ on drying or long aging. Such highly crystalline $PuO_2 \bullet 2H_2O$ cannot be depolymerized and is very difficult to re-dissolve. There is no information in the literature on the effect of agitation on adsorption. It is possible the thickness of the adsorbed polymer layer may be thinner; however, it is unlikely that agitation will remove polymer once it has adsorbed onto the steel. The initial layers of polymer are adhered to the surface as a thin layer and should not be considered as part of the 45 g limit for Pu solids in H-Canyon. No information is available in the literature to determine how thick the layer of Pu polymer can get before cracking and flaking would occur. That information will be determined in laboratory tests on adsorption.

As explained above, Pu polymer changes from a hydroxide to crystalline $PuO_2 \bullet 2H_2O$ during the aging process. The crystalline material does not have a charge on the surface and proceeds to precipitate. The solids are produced uniformly throughout the solution. The particle size averages 20 microns.[16] Mixing studies at SRTC have shown that particles of similar density up to 50 microns in size were completely and uniformly suspended at an agitator speed of 68 rpm in process vessels.[36] In fact, such particles can be re-suspended uniformly in solution even after settling has occurred.

Low acid/water addition can occur either intentionally or unintentionally during operations. Intentional additions include transfers from scrubber tanks or sump tanks and addition of water by the steam jet during tank-to-tank transfers. Unintentional additions are mostly in the form of leaks from cooling coils or jackets. The acid concentration in the receipt tank can be raised before the transfer in the case of intentional additions. However, cooling water leaks into tanks are rare and cannot be predicted in advance so preparing a tank is difficult. A part of the defense against polymer formation due to leaks must consist of quickly determining that a leak has occurred so that appropriate actions can be taken to determine whether polymer has formed. The operating area defined should be capable of preventing problems in either case. To clearly delineate application of the literature information, various scenarios are shown in Table 1. Each of the scenarios will be discussed along with how to recover if polymerization does occur.

Canyon floors and sumps are flushed on a regular basis to ensure that leaks and spills of Pu solutions do not lead to unsafe accumulation of Pu. The floors are flushed with water and the water is pumped to the sump receipt tank for analysis and subsequent treatment or disposal as waste. Flushing uses large quantities of water relative to the acid on the floors or in the sumps. If the Pu has dried out and converted to PuO_2, the solids will be transferred into the tank. If the Pu is still in solution or is present as Pu nitrate, it is possible that polymer will be formed if the acid concentration in the flush solution is <0.1 M. If the acid concentration is less than 0.01 M, polymerization and precipitation could be immediate but the particle size of the solids will be small and will be transferred to the sump tank. In either case, the total mass of Pu is less than a critical mass unless multiple transfers over a period of weeks or months are collected before emptying the tank. Pu polymer can be depolymerized by increasing the acid concentration to > 4 M within a day after the transfer. Some of the polymer can adsorb onto the sump, transfer pipe, and tank walls if allowed to age for 1-2 days. Sampling and analysis within a day should allow any polymer formed to be detected and acid added to depolymerize safely.

Table 1. Scenarios for Polymer Formation

Scenario	Pu Content	Initial HNO_3, M	Polymer Formation
Water flushes of sump and collection in receipt tank.	<450 g total	<0.1 in sump	Polymer can form, but can be depolymerized with >4M acid if done within one day.
Water additions to evaporator and evaporator feed tank	<0.1 g/L	0.1- 8	Polymer forms at low acid, but depolymerizes during evaporation.
Scrub or other low acid solutions added to tank	≤7 g/L	0.2-4	Polymer forms with precipitation rate dependent on acid.
Slow cooling water leak into tank (7 days to detect, 1 % volume increase)	≤7 g/L	0.2-8	Possible polymer at < 4 M acid. Depolymerizes without precipitation at >4 M final acid.
Rapid cooling water leak (≤ 1 day to detect, 1 % volume increase)	≤7 g/L	0.2-8	Polymer formation with rapid depolymerization at > 4 M final acid.
Slow cooling water leak into tank (7 days to detect, 10 % volume increase)	≤50 g/L	0.5-8	Polymer formation with rapid depolymerization at > 4 M final acid.
Rapid cooling water leak (≤ 1 day to detect, 10 % volume increase)	≤50 g/L	0.5-8	Polymer formation with rapid depolymerization at > 4 M final acid.
Steam jet transfer	≤7 g/L	0.2-8	Possible polymer at < 4 M acid. Depolymerizes without precipitation >4 M final acid.

Rain water and other miscellaneous very low acid streams are routinely added to evaporator feed tanks and then sent to the evaporator for concentration. Polymer can form during addition of the water to the tank if the acidity goes to 0.01 M or lower even if the low acidity is a transient of short duration. Even with the agitator operating, it is possible to have such transient conditions. The typical Pu concentration in the evaporator feed tank is ≤ 0.02 g/L. Polymer formed at low Pu concentration is reported to be stable in solution for 6 or more days before precipitation.[23] As the solution ages, some of the polymer can be adsorbed onto the walls, agitator and coils in the tank. The thin layer of Pu adsorbed to the walls can be removed periodically by hot 8-10 M HNO_3 with fluoride ion. Any polymer remaining in solution will be transferred to the evaporator. Polymer formation and aging are much more rapid at high temperatures; however, solutions are typically evaporated to 4 M acid, which at high temperature should re-dissolve the polymer as well as maintain the walls free of adsorbed polymer. Certainly repeated evaporations should keep the walls of the evaporator free of adsorbed Pu. The Pu in the evaporated solution is transferred to waste neutralization where the presence of solids is expected and controlled to safe levels.

Scrubbers in the B lines contain neutral or low acid solutions, which must periodically be dropped to a canyon tank for disposal. Addition of such solutions to Pu solutions with high Pu concentration (1-7 g/L) are likely to form some polymer during the addition due to transient low acid conditions as discussed earlier for evaporator feed tanks. However, the higher Pu concentration means that polymerization occurs at higher acid concentration. If the final acid concentration is less than 0.2 M, polymer formation will occur in a period of several days. When the final acid concentration is in the range of 1 to 4 M, the polymer depolymerizes with the rate of depolymerization depending on the acid concentration. Depolymerization of any polymer formed is ensured when the final acid concentration is 4 M or higher.

Cooling water leaks can possibly occur for tanks in the canyons. The pressure of cooling water for all tanks is maintained higher than the pressure in the tank so that any leaks will be into the tank not into the cooling water system. A pinhole leak would be expected to leak at a rate that would be slow enough that several days to a week would be necessary to observe the change in tank level. Canyon procedures require a level check every shift. A change of 1 % in level instrumentation (about 1-2 inches of water pressure for most tanks and 3 inches for bicells) since the last liquid addition indicates a cooling water leak into the tank. The cooling water is not acidified so there is possibility for polymer formation. A 1 % increase for the level instrumentation corresponds to about 400 liters of water over a period of 2 to 7 days. That volume is not enough to change the overall acid concentration of a half to completely full tank. However, in a tank with only a heel present, the acid concentration could be reduced to a third of the initial concentration. Polymer will form as the water enters the tank. Polymer formation will be more extensive at acid concentrations close to the minimum allowed by the safety basis. Polymer formation should decrease as the acid concentration increases. Polymer formation would be unlikely in full tanks with acid concentration > 4 M. Polymer formation is also minimized if the agitator is operating except in the case of a leak into a heel where the liquid level is too low to be mixed by the agitator. If polymer were to form, it could be depolymerized depending on the final acid concentration as stated in the previous paragraph. It is likely with a slow leak that a significant portion of the polymer would age and adsorb to the surfaces of the tank where depolymerization will be slow except at high acid with fluoride catalyst. Such thin layers of Pu should not be a nuclear safety concern and should not be considered as part of the solids limit for the tank.

Cooling water leaks, which are observed in one or two shifts, add the same total amount of water into the tank in a much shorter time and are more likely to result in polymer formation as a result of transient low acid concentrations even with agitation. It should be noted that a rapid leak could provide some mixing of the solutions and thus form less polymer than with a slower leak. The following are suggestions for safe handling of solutions where a leak has occurred and polymer may have formed. The solution should be transferred from the tank to prevent further dilution as soon as a leak is detected. The solution should be sampled and analyzed for Pu polymer within one day of observing the leak, if the acid concentration is < 4 M. If Pu polymer is observed in the sample, acid and/or fluoride can be added to help depolymerization. Care must be taken in adding acid to solutions of 0.5 to 1 M HNO_3 because the literature shows that precipitation can occur during acid addition. In such cases, acid addition should be carried out with agitation to keep the solids suspended and the final acid concentration should be > 4 M for rapid depolymerization or dissolution. Agitation should be continued for several days to allow depolymerization of precipitate (see Figure 7) before sampling and analysis for solids containing Pu. If the acid concentration is > 4 M, no action is required because the rate of depolymerization is rapid.

The HB-Line has some tanks, which could have up to 50 g/L Pu solution and are jacketed with cooling water. Differences in tank size and instrumentation result in dilution up to 10 % of volume in order to detect a leak. With a slow leak, polymer formation is likely at these high concentrations due to transient low acidity at the leak point although agitation should minimize the amount. As stated for canyon tank leaks, the polymer will likely be aged by the time the leak is confirmed and precipitation is likely if acid is added to 0.5 to 1 M solutions. Final acid concentration > 6 M would result in depolymerization of any polymer formed as stated earlier, however, the polymer has aged and depolymerization is not rapid (see Figure 7). Solutions where leaks are confirmed can be safely treated by sampling and analyzing for polymer while maintaining agitation in the tank. Increasing the acid concentration well above 4 M (see Figure 7) and stirring for a week or more should depolymerize any polymer formed.

A rapid leak into a HB-Line tank would result in polymer formation. Such leaks should be treated the same as for slow leaks as given in the previous paragraph.

Another way that polymer could potentially be formed is during tank to tank transfers via steam jet. Historically, plutonium polymerization in a steam transfer jet has not been a processing problem.[37] Based on experience gained at the Savannah River Plant, acidified steam was not required during transfers. Separately, Toth and Dodson[25] report experimental steam-jet transfer results in which "solutions with $[HNO_3] > 1.0M$ showed no signs of polymer formation even when the concentration of the Pu(IV) was as high as 0.35 M." Lee[37] calculated the plutonium polymer formation in a commercial jet based on research done at Oak Ridge[17] and on manufacturer's data. The jet dilution is 2-3 % and the residence time in the jet is less than 0.6 sec. Lee's calculations showed that for plutonium solutions of at least 0.1M in HNO_3, a negligible amount of polymer formed. Calculation of the temperature increase of the solution during transfer shows a 15-20°C temperature rise. Therefore, any solution at ambient canyon temperature would not be expected to exceed a temperature at which polymer would form.

Performance curves for seven different steam jets[38] were used to calculate the degree of dilution and the temperature rise of the solution due to steam condensation during transfer. Calculations were made at different steam pressures, lift and discharge head requirements. In all cases, dilution was 2 to 3 %. The highest temperature rise was 37°F (20.5°C). A sample calculation follows.

For a Z6 (Penberthy QRS) Rate Jet with 80 psig steam, HNO_3 solution is transferred at 9.2 gpm when a lift of 12.0 ft H_2O and a discharge head of 19.0 ft H_2O are required. During one hour of steady-state operation, 552 gal = 2090 liters = 4600 lbs of solution are transferred. (Though calculations were done for one hour, they describe the temperature rise and dilution expected for steady-state operation over any length of time.) The steam consumption is 152 lbs. From steam tables, the enthalpy change due to condensation (and cooling) of the steam is 1118.1 BTU/lb*152 lb = 1.7×10^5 BTU. The temperature change is given by $\Delta H = m\,C_p\,\Delta T$. Using a heat capacity of 1 BTU/lb°F, the temperature rise of the solution is $\Delta T = 1.7 \times 10^5$ BTU/(4600 lbs)(1 BTU/lb°F) = 37°F (=20.5°C). This was the highest temperature rise calculated for a group of seven steam jets under multiple conditions. The same steam jet operated with 110 psig steam would yield a temperature rise of only 16°C. Only in the summer are tank solutions likely to be 35°C or higher. It follows that the great majority of steam jet transfers in F and H-Canyons and B-Lines are not likely to raise the temperature of a plutonium/ HNO_3 solution high enough (above 50°C) to form polymer. This is the main reason why polymer formation due to steam jet transfers has not been observed.

In rare cases, the dilution caused by steam jet transfers has reached 7%.[39] In such cases, Pu(IV) polymer will not form if the acid concentration is ≥ 0.4 M (see Figure 4). At lower acid concentrations, the receiving tank should be cooled or acidified to prevent Pu(IV) polymer formation. A third alternative is adding small amounts of complexing agents (i. e., SO_4^{2-}). Rainey[27] stated that SO_4^{2-} prevents polymer formation associated with hot spots in evaporators or steam jets.

In summary, Pu(IV) polymer formation has not been a problem, historically, in steam jet transfers. This is mainly due to the fact that a minimum HNO_3 concentration has been maintained. Experiments using 1 M HNO_3 solutions showed no polymer formation for Pu(IV) concentrations up to 84 g/L (0.35 M).[25] For steam jet transfers involving high lift (e.g., 12 ft) and significant discharge head requirements, the temperature rise and dilution could lead to polymerization. Cooling or acidifying the solution would prevent polymer formation. Precipitation and possibly adsorption of polymer on the tank walls depend on the time of aging and the final acid concentration in the tank. As noted in the section on chemistry, addition of acid to a solution where polymer has already formed can lead to precipitation. Thus, Pu containing solutions, which have inadvertently been diluted to acid concentrations below the minimum in the safety basis documents, should be analyzed for polymer before addition of acid to increase the concentration.

Recommendations

1. Maintain a minimum acid concentration of 0.22 M during storage of Pu solutions with up to 7 g/L at ambient temperature.
2. Maintain a minimum acid concentration of 0.4 M during storage of Pu solutions with 7-50 g/L at ambient temperature.
3. Addition of solutions containing less than 0.1 M HNO_3 to Pu solutions with ≥ 0.1 g/L Pu should be avoided except for solutions with > 250 g/L U or where the final acid concentration is ≥ 4 M HNO_3.
4. Agitators should be operating whenever low acid additions are made to any tank.
5. If Pu polymer is found, one way of handling the solution is to raise the acidity above 4 M, preferably to 6 M HNO_3, in order to depolymerize.

Experimental data to confirm the temperature and nitric acid concentration necessary to remove adsorbed polymer would be helpful. Solutions at the specified conditions could then be used to remove polymer, which might be adsorbed by tanks.

Conclusions

The chemistry of Pu polymer formation, precipitation, and depolymerization is complex. Establishing limits on acid concentrations of solutions or changing the valence to Pu(III) or Pu(VI) can prevent plutonium polymer formation in tanks in the B lines and canyons. As shown in Figure 4 for Pu(IV) solutions of 7 g/L or less, 0.22 M HNO_3 prevents polymer formation at ambient temperature. This should remain the acid limit for the canyons and B lines when processing Pu-239 solutions. If the minimum acid concentration is compromised, the solution may need to be sampled and tested for the presence of polymer. If polymer is not detected, processing may proceed. If polymer is detected, adding HNO_3 to a final concentration above 4 M is the safest method for handling the solution. The solution could also be heated to speed up the depolymerization process. Heating with ≥ 4 M HNO_3 will depolymerize the solution for further processing.

Adsorption of Pu(IV) polymer onto the steel walls of canyon and B line tanks is likely to be 11 $\mu g/cm^2$, a literature value for unpolished steel. This value will be confirmed by experimental work. Tank-to-tank transfers via steam jets are not expected to produce Pu(IV) polymer unless a larger than normal dilution occurs (e.g., >3%) at acidities below 0.4 M.

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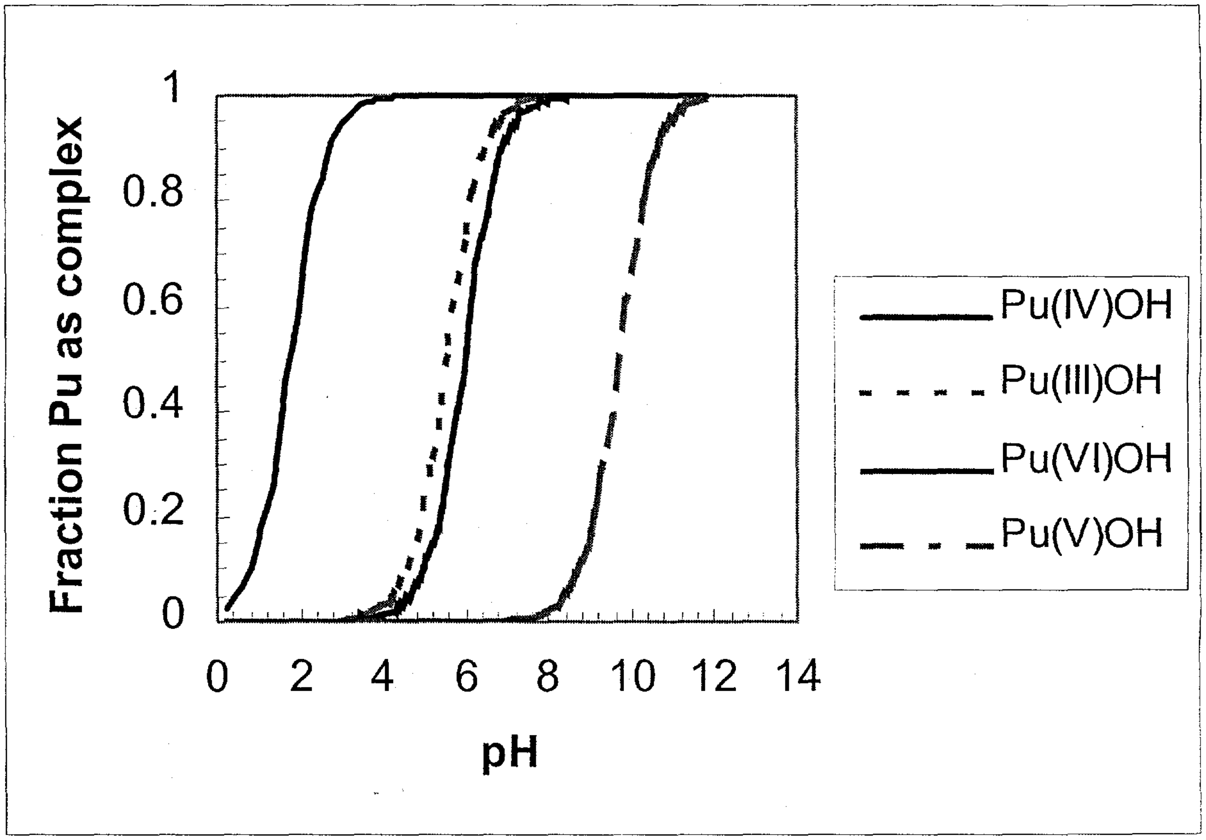

Figure 1. Onset of plutonium hydrolysis calculated as a fraction of the total Pu concentration using stability constants for monohydroxy Pu complexes.[4]

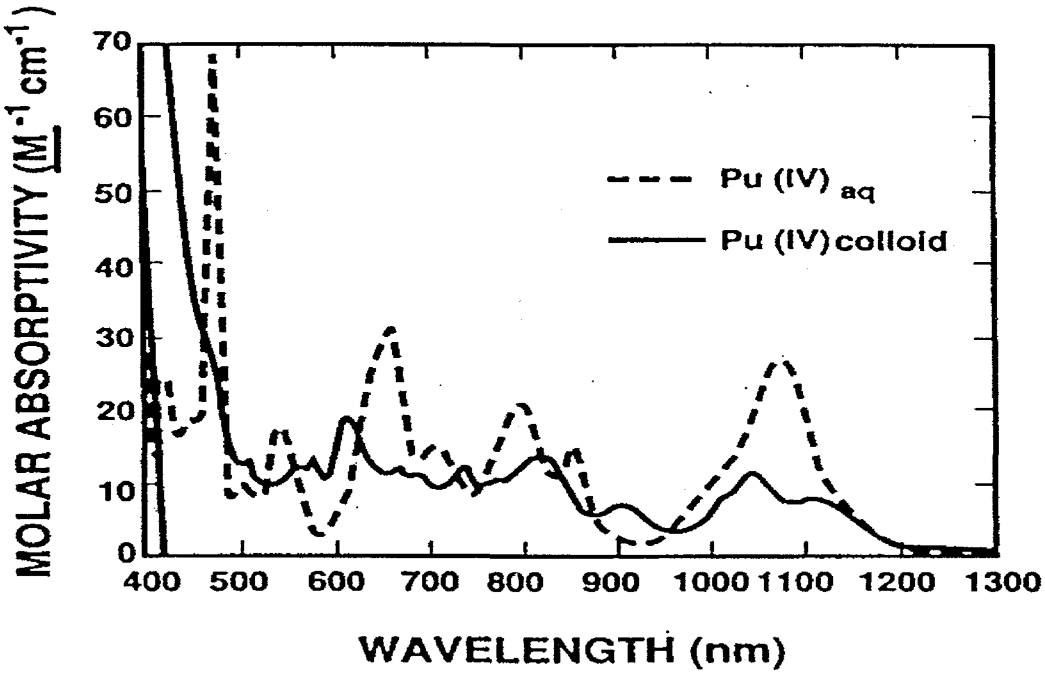

Figure 2. Absorption spectra of Pu(IV) and Pu(IV) polymer solutions.[5]

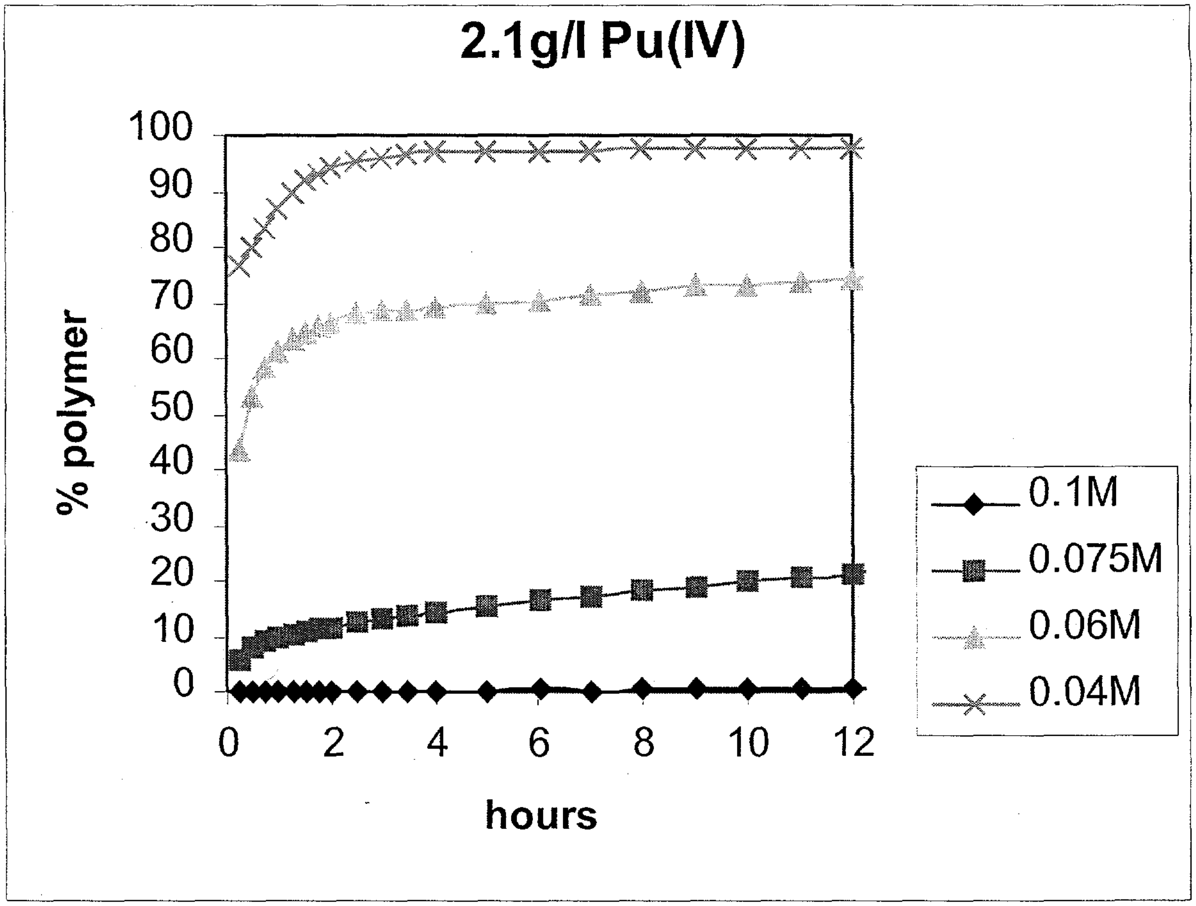

Figure 3. Rate of polymerization for 2.1g/L Pu in HNO_3.[17]

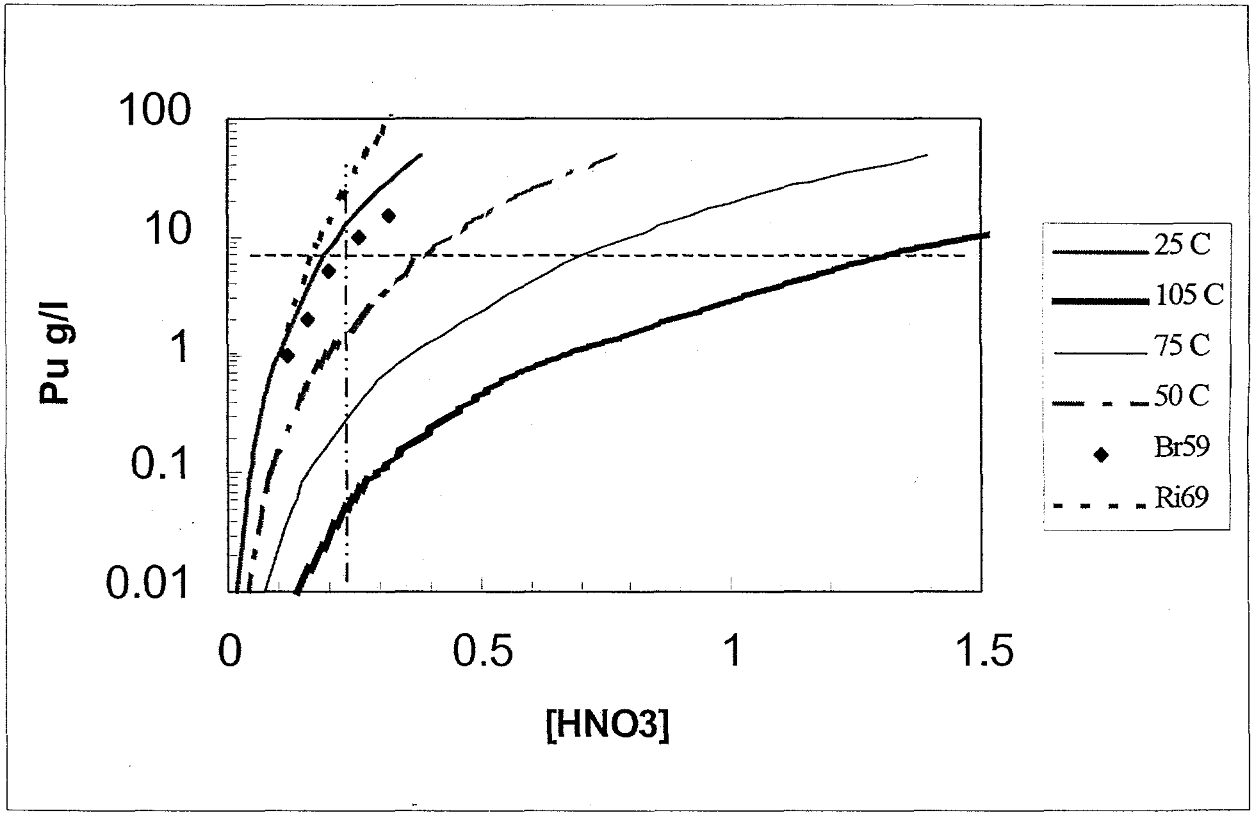

Figure 4. Effect of temperature on minimum HNO_3 concentration required to prevent polymer formation calculated from empirical equations 7^{25} and 8^{26}. Equation 8 values, labeled Ri69, were calculated at 25°C. Experimental data labeled Br59 is from Brunstad.[7] The horizontal dashed line at 7 g/L Pu and the vertical dot dashed line at 0.22 M are process limits.

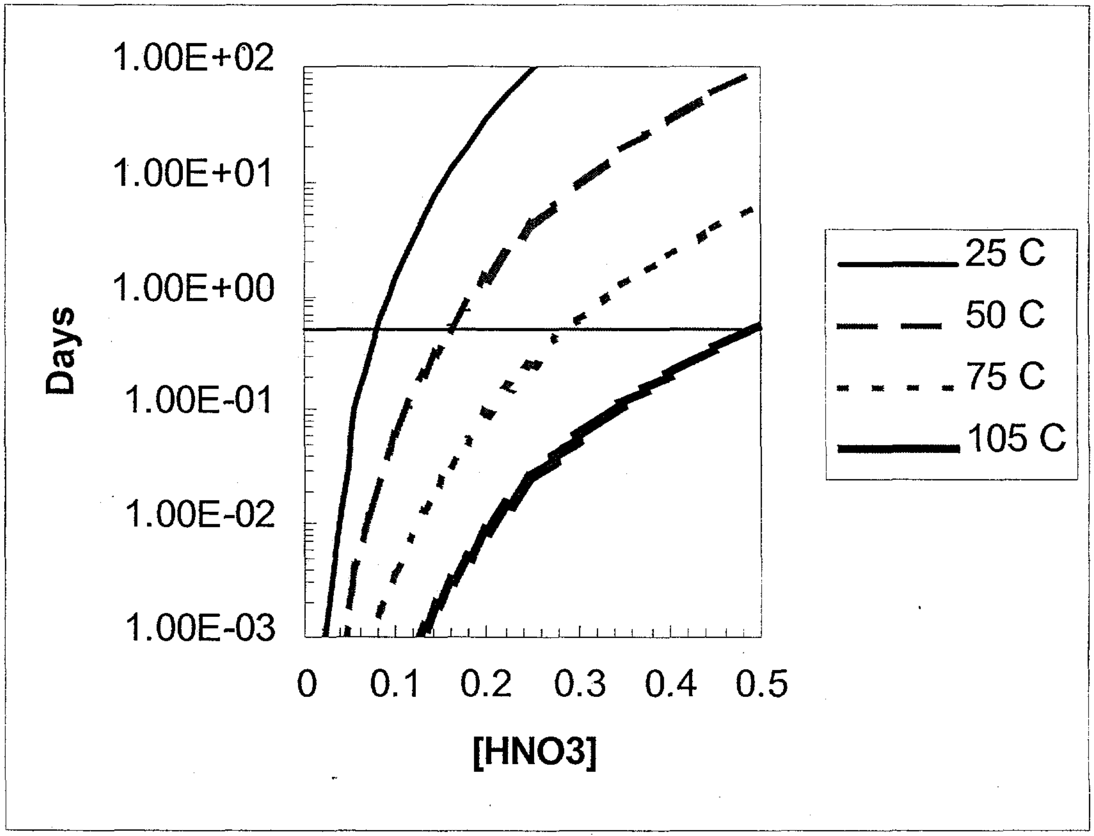

Figure 5. Rate of 2% polymer formation at 2g/L Pu as calculated from equation 7.[25]

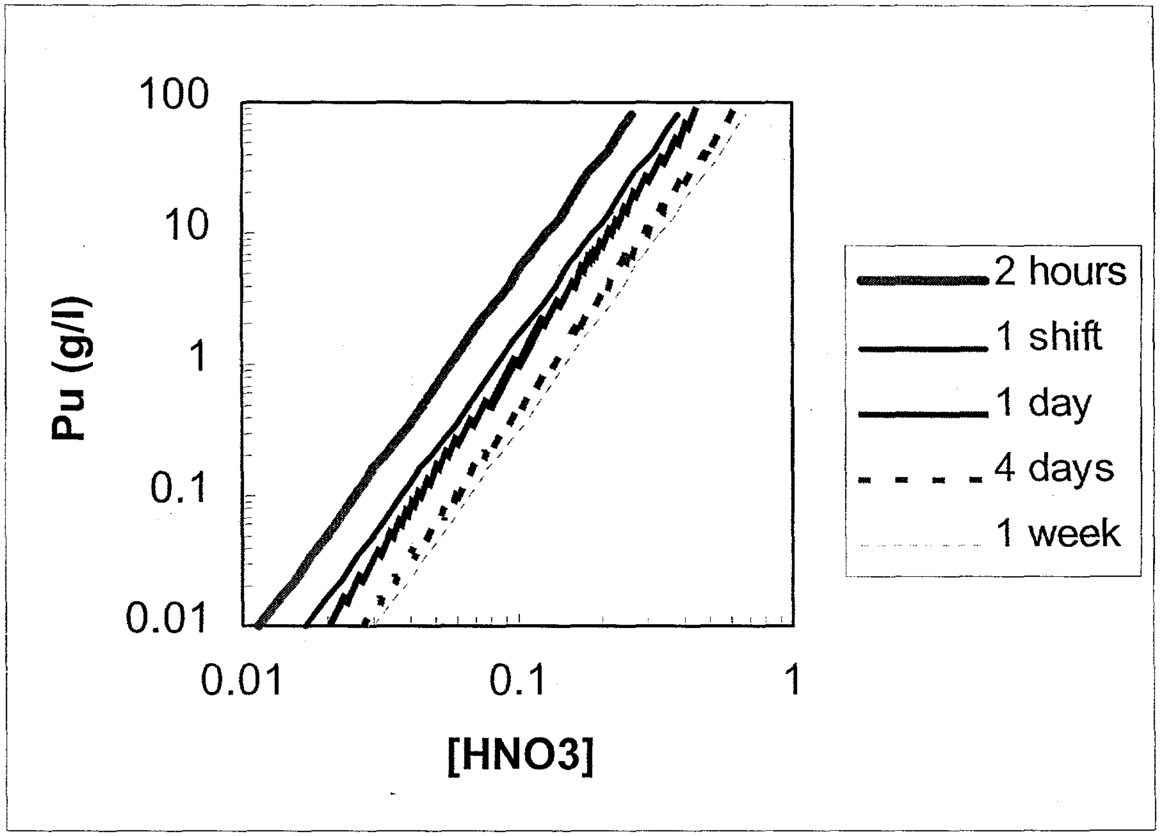

Figure 6. Rate of polymerization at 35°C as a function of Pu concentration as calculated from equation 7.[25]

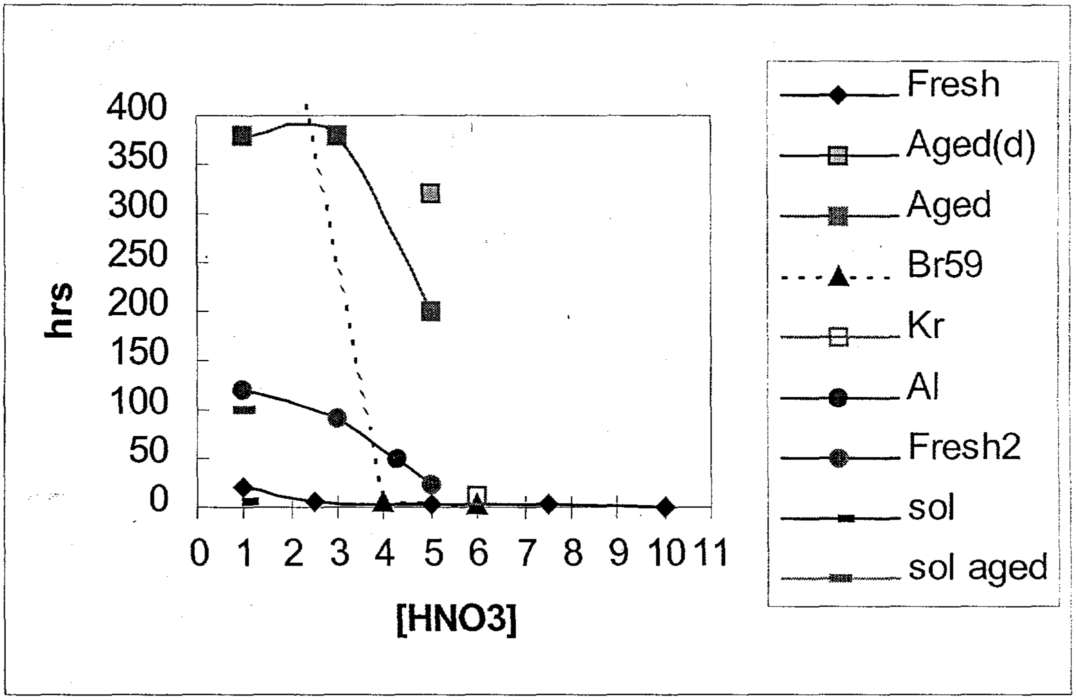

Figure 7. Depolymerizaton half times of fresh and aged Pu polymer at room temperature or 25°C. Fresh polymer values are labeled Fresh[8], Br59[7], Fresh2[29], and sol.[13] Aged polymer values are labeled Aged(d)[8], Aged[29], Kr[27], Al[27], and sol aged.[13] Values labeled Aged were determined at 18°C.