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Sonochemical Digestion of High-Fired Plutonium Dioxide Samples

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Summary

This work was performed as part of a broader effort to automate analytical methods for determining plutonium and other radioisotopes in environmental samples. The work described here represented a screening study to evaluate the effect of applying ultrasonic irradiation to dissolve high-fired plutonium oxide. The major findings of this work can be summarized as follows:

- High-fired PuO_2 does not undergo measurable dissolution when sonicated in nitric acid solutions, even at a high concentration range of HNO_3 where the calculated thermodynamic solubility of PuO_2 exceeds the µg/mL level.

- Applying organic complexants (nitrilotriacetic acid) and reductants (hydroxyurea) in 1.5 M HNO_3 does not significantly increase the dissolution compared with digestion in nitric acid alone. Nearly all (99.5%) of the PuO_2 remains undissolved under these conditions.

- The action of a strong inorganic reductant, $TiCl_3$ in 25 wt% HCl, results in 40% dissolution of the PuO_2 when the $TiCl_3$ concentration is ≥ 1 wt% under sonication.

- Oxidative treatment of PuO_2 by freshly dissolved AgO (~20 mg/mL) in 1.5 M HNO_3 with sonication resulted in 95% PuO_2 dissolution. However, the same treatment of PuO_2 mechanically mixed with 50 mg of Columbia River sediment (CRS) results in a significant decrease of dissolution yield of PuO_2 (<20% dissolved at the same AgO loading) because of parasitic consumption of Ag^{2+} by oxidizable components of the CRS.

- Digesting PuO_2 in HF resulted in dissolution yields slightly higher than 80% for HF concentration from 6 M to 14 M. Sonication did not result in any improvement in dissolution efficiency in HF.

- Mixed nitric acid/HF solutions result in a higher dissolution yield of PuO_2 compared with digestion in HF alone (at the same HF concentrations). Practically quantitative dissolution of PuO_2 can be achieved with 6 to 8 M HNO_3 + 14 M HF or 8 M HNO_3 + 4 M HF mixtures. In the latter case, quantitative dissolution of PuO_2 was demonstrated only with sonication.

Overall, the results indicate that applying ultrasound in an isolated cup horn configuration to dissolve refractory PuO_2 does not offer any substantial advantage over conventional "heat and mix" treatment. Oxidative treatment by AgO appears to be effective only when very little or no oxidizable materials are present in the digested sample. The catalytic use of Ag^{2+} in the "Catalyzed Electrolytic Plutonium Oxide Dissolution" technology would probably be more effective than using AgO because the Ag^{2+} is continually regenerated electrochemically. Reductive treatment with $TiCl_3$ in HCl solution proves to be less efficient than the previously observed effect based on *in situ* generation of Ti^{3+} in H_3PO_4 and H_2SO_4 media using a dip probe sonication setup. The previous experiments, however, were performed at higher temperature and with non-steady concentration profiles of Ti^{3+} in the process of sonochemical digestion.

Acronyms

CEPOD   Catalyzed Electrolytic Plutonium Oxide Dissolution

CRS   Columbia River Sediment

DI   deionized (water)

HF   hydrofluoric acid

HNO_3 nitric acid

HU   hydroxyurea (HO-NH-C(O)-NH_2)

LSC   liquid scintillation counting

NIST   National Institute of Standards and Technology

NOM   natural organic matter

NTA   nitrilotriacetic acid [N-(CH_2-COOH)$_3$]

SRM   standard reference material

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1.0 Introduction

The application of ultrasound in chemistry (i.e., sonochemistry) has evolved over the last two decades. Introducing ultrasonic waves into a liquid such as water creates microbubbles that collapse implosively, forming localized "hot spots." This phenomenon is generally referred to as *cavitation*. The interesting feature of the cavitation effect is that the temperatures in the hot spots are roughly 5000°C with pressures of several hundred atmospheres, but the bulk solution conditions remain at near ambient conditions (Suslick 1988). The extreme localized temperature and pressure conditions caused by acoustic cavitation can open up reaction pathways that are not easily accessible otherwise.

In our previous study on the enhancement of Pu(IV) colloids and dioxide dissolution by sonochemistry[a] using a dip horn configuration of the sonicating probe, we observed, among other things, that:

- Sonication was found to significantly increase the dissolution of low-fired PuO_2 in 2.5 M H_3PO_4 or 2.5 M H_2SO_4. Sonication increased the rate of dissolution by ~300-fold. High-fired PuO_2 was also investigated and found to be more resistant to dissolution with better leaching efficiency obtained in sulfuric acid solution.

- The appearance of purple color in these systems suggests the formation of Ti^{3+} because of minor corrosion of the ultrasonic probe. The role (if any) of Ti^{3+} in the oxide dissolution was not determined in the prior work.

In those experiments, a titanium sonicating horn was directly immersed into solution. A significant enhancement in dissolution efficiency of low-fired PuO_2 was observed in phosphoric and sulfuric media only, and it was accompanied by the progressive appearance of the purple color characteristic of Ti^{3+} during sonication. No coloration was observed in the nitric acid solution, and no significant dissolution of PuO_2 under sonication was observed in HNO_3 (<0.5% of total dissolved alpha activity in solution). At that stage, it was concluded that future studies should explore the impact of changes to the sonochemical equipment with particular emphasis on systems in which the probe is not directly inserted into the reaction medium; this would avoid corrosion of the probe and cross-contamination of the solutions. It was also suggested that control experiments should be conducted on the dissolution of PuO_2 in H_3PO_4 and H_2SO_4 solutions in which Ti^{3+} is added to determine the extent to which Ti^{3+} participates in the dissolution mechanism.

The aim of the current project has been to further explore the potential advantages of sonication in enhanced dissolution of refractory PuO_2 in acidic media to determine the role of various complexing, reducing, and oxidizing agents using a modified sonicating instrument based on a cup horn sonication geometry as opposed to the previously tested dip probe configuration.

(a) GJ Lumetta, SI Sinkov, and JI Friese. 2005. *Enhancing Actinide Separations by Sonochemistry* (FY 2005 Report, Unpublished Manuscript).
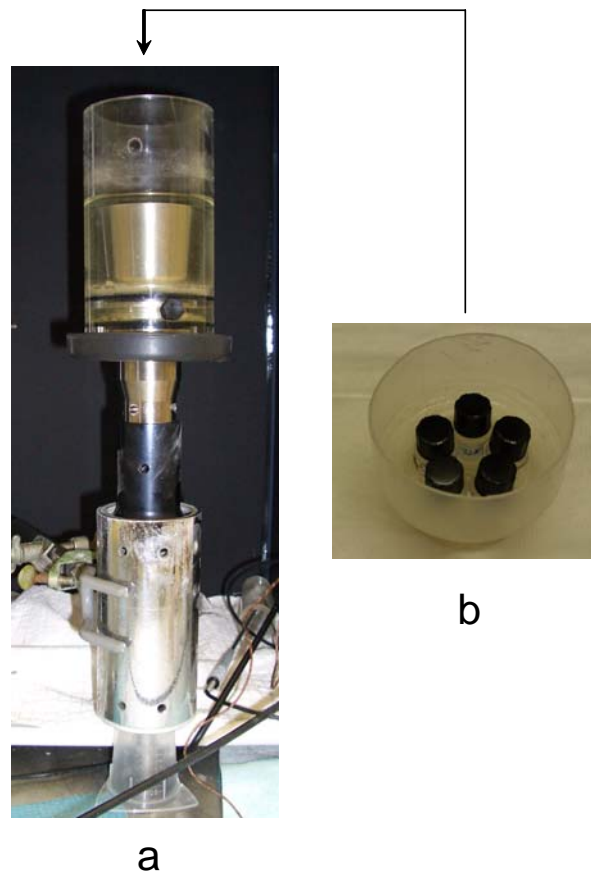
2.0 Experimental

The sonication apparatus consisted of a 2-inch-wide cup horn coupled to a Model CL4 converter (20 kHz), which was driven by a Model XL-2010 power supply (all equipment was obtained from Misonix, Inc.; formerly Heat Systems, Farmingdale, New York). The use of the cup horn configuration avoids contact of the sample with metallic components (as would be the case for a dip horn) that might interfere with subsequent analytical procedures. Figure 2.1 illustrates the experimental apparatus. The sonicator was operated at a starting power output of 46% (power dial setting 4.0 in the scale of 1 to 10). No means were taken to maintain constant temperature during the experiments, but under the conditions used (0.5- to 0.75-inch-thick water layer above a top surface of the sonicating horn), the temperature typically reached 80°C within the first 40 minutes of sonication with an additional rise to 84°C over the next 20 min. Figure 2.2 shows the detailed temperature profile in the sonication sample compartment. Control experiments were performed using a heated water bath with a capacity for five vials with a heating mode resembling the sonication temperature profile. Occasional mechanical stirring was applied to agitate the control samples during digestion. Glass and plastic vials of 4-mL capacity were used for digestion experiments in HF free media and in the presence of HF, respectively. Contact times of 1 hr were employed in all sonication and control experiments.

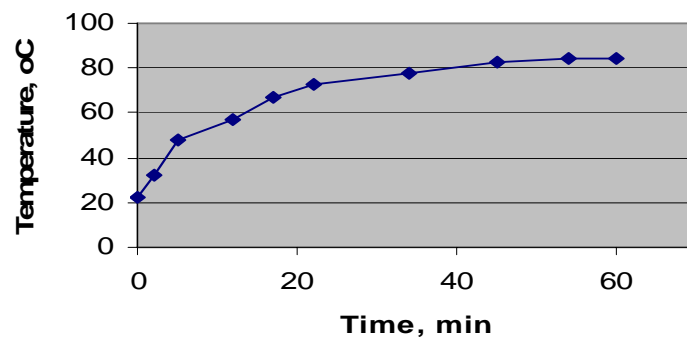## 2.1 PuO$_2$ Preparation and Subsampling for Dissolution Experiments

High-fired PuO$_2$ was prepared by calcination of a small amount of low-fired PuO$_2$ in a muffle furnace at 1000°C for 4 hrs. Several nominally 1-mg portions of the calcination product were weighed out using a five-place balance (LE 222D, Sartorius) setup in a glovebox. Their weight was determined with a 10-μg uncertainty. The pre-weighed portion of PuO$_2$ was transferred into a fume hood where it was mixed with deionized (DI) water (in a 1.00 mg PuO$_2$ to 1.50 mL H$_2$O ratio) to prepare aqueous suspensions of this material suitable for safe handling in a fume hood. Portions of PuO$_2$ (~33 μg of the material) used in the digestion experiments were produced by pipetting 50-μL aliquots out of the stock suspension vial. The transfer was carried out under constant magnetic stirring (400 rpm) of the suspension to eliminate concentration gradients within the volume of the stock solution, which otherwise would develop without agitation because of quick sedimentation of the high-density powder of PuO$_2$ in water.

2.2 Calculation of Specific Alpha Activity of $^{239,\,240}$Pu

The PuO$_2$ used in this project represented a mixture of ^{239}Pu (93.85%), ^{240}Pu (5.98%), and ^{241}Pu (0.22%) with traces of ^{238}Pu and ^{242}Pu. Plutonium-241 is a beta-emitter with a relatively short half life of 14.4 years. It does not contribute directly to the total alpha-activity from other Pu isotopes in this mixture, but its decay product, ^{241}Am, does. Because no information was available on the date of the last purification of this Pu sample from ^{241}Am, an assumption was made that 50% out of the initial 0.22% of ^{241}Pu had decayed into the daughter product. This assumption corresponds to one half life of ^{241}Pu or 14.4 years since the last purification from ^{241}Am. Two other extreme cases (complete absence of ^{241}Am and 100% conversion of ^{241}Pu into ^{241}Am) would change the total specific activity of this mixture of Pu isotopes by ±4.6%. The calculated specific activity of this particular Pu sample is 2.87×10^6 Bq/mg of Pu (as Pu metal). This value is 25% higher than the one based on the frequently used simplified assumption that all specific activity in the weapons-grade plutonium can be attributed solely to ^{239}Pu.

Figure 2.1. a, left) Sonication Apparatus in a Cup Horn Configuration Used in this Project; b, right) Self-Centering Vial Holder

Figure 2.2. Temperature Profile Measured Inside of a Cup Horn Water Bath During 60 min of Sonication Run at 46% of Full Power (dial setting at 40% of full scale)

2.3   Reagents

All solutions were prepared using DI water as a solvent. Nitric acid and HCl were of trace metal grade purity. Titanium trichloride solutions (in the Ti^{3+} concentration range of 0.5 to 2 wt%) were prepared by diluting a 10 wt% $TiCl_3$ stock solution in 20 to 30 wt% HCl (Sigma-Aldrich) with a 25 wt% HCl solution. Hydroxyurea (98% purity), AgO, and nitrilotriacetic acid (99%) were obtained from Aldrich Chemical Company.

2.4   Digested Sample Pretreatment and Filtration

A syringe filtration technique was employed to separate unreacted PuO_2 from the dissolved plutonium before determining the amount of dissolved plutonium by liquid scintillation counting (LSC). A 0.20-μm Nylon membrane filter was used for this purpose. If the acidic sample contained HNO_3 or HCl at a concentration of 3 M or higher, the original post-digested sample was diluted with DI water to reduce acidity to 2 M to protect the membrane filter material from destruction in the strongly acidic medium.

2.5   LSC Counting

A Tricarb liquid scintillation analyzer (Model 2500 TR) was used to measure the total alpha activity ($^{239}Pu + {}^{240}Pu + {}^{241}Am$) in leachates by spiking an appropriate liquid sample aliquot into 4.0 mL of Ultima Gold XR liquid scintillation cocktail (Packard Instruments).

2.6   Control Experiment

In those cases where sonication showed a significant degree of PuO_2 dissolution, control experiments were performed with conventional heat and mix equipment following approximately the same temperature profile as the one observed during the sonication experiments (see Figure 2.2).

2.7   Dissolution Efficiency Determination

The total activity of the dissolved Pu in the digested sample was determined by multiplying the value of the observed activity in the LSC sample by the dilution factor and by the sub-sampling factor (that is, the ratio of the total volume of liquid in the digested sample [typically 1 mL] to the volume of this solution taken for analysis). The determined value of the total activity was then compared with the calculated activity of $^{239,240}Pu$ expected to be present in solution in case of complete dissolution of the PuO_2.

3.0 Results and Discussion

This section discusses the dissolution of high-fired PuO_2 in HNO_3 solutions of various acidity: 1) a solution of nitrilotriacetic acid (NTA) in 1.5 M HNO_3 (representing a strong organic complexant favoring the tetravalent state of Pu in acidic solution), 2) a solution of hydroxyurea (HU) in 1.5 M HNO_3 (representing an organic reductant favoring a +3 oxidation state of Pu in solution), 3) a solution of $TiCl_3$ in HCl (representing a strong inorganic reductant favoring Pu(III) in solution), 4) a 1.5 M HNO_3 solution in the presence of AgO (representing a strong inorganic oxidant favoring Pu(VI) in solution), and 5) mixtures of HF and HNO_3 (using fluoride as a powerful inorganic complexing and dissolving agent for Pu(IV) compounds). Contact times of 1 hr were employed in all sonication and control experiments described in this section.

3.1 PuO_2 Dissolution in HNO_3

Two sets of sonication experiments were performed in HNO_3 solutions of variable concentration. In the first set, five samples with HNO_3 concentration from 2.0 to 8.3 M were digested, and in the second set, five more samples were processed in the 9.0 to 15.8 M concentration range of HNO_3. No appreciable dissolution was observed for any of the 10 concentrations tested. The best result of 0.57% total dissolved alpha activity was achieved for the 9.0 M HNO_3 solution. The average dissolved fraction for all 10 samples was found to be 0.19 ± 0.16%. No control experiments were performed in this case because no significant dissolution was achieved with sonication.

3.2 PuO_2 Dissolution in Nitrilotriacetic Acid Solution in 1.5 M HNO_3

Solutions of NTA in 1.5 M HNO_3 with NTA concentrations ranging from 5 mM to 25 mM were tested for dissolving PuO_2 under sonication. NTA is a powerful complexing agent for tetravalent actinides (Sinkov and Lumetta 2006), and it was expected that it may exhibit a good leaching capability for PuO_2. In reality, the maximum dissolved fraction of PuO_2 observed in our experiments was less then 0.6%, which was obtained with 20 mM NTA; the average value was 0.27 ± 0.18% for all five samples tested with this reagent. So NTA/HNO_3 does not appear a promising medium for dissolving high-fired PuO_2.

3.3 PuO_2 Dissolution in the Presence of Hydroxyurea in 1.5 M HNO_3

It has been reported recently that HU can be used as a novel salt-free reductant in nitric acid solutions for conversion of Pu(IV) to Pu(III) (Zhaowu et al. 2004). It exhibits superior kinetics over hydroxylamine and its organic derivatives. We tested this reagent in 1.5 M HNO_3 solution for reductive leaching of PuO_2 with HU concentrations in the range 40 to 200 mM. No significant dissolution was observed with this reagent with or without sonication. The best result was achieved for an HU concentration of 80 mM (1.0 wt%), while the average efficiency for the entire series was found to be 0.33 ± 0.40%.

3.4 PuO_2 Dissolution in the Presence of $TiCl_3$ in 25% HCl

In our previous report, *Enhancing Actinide Separations by Sonochemistry,*[a] we achieved practically quantitative dissolution of low-fired PuO_2 in 2.5 M H_2SO_4 and 2.5 M H_3PO_4 using an emersion probe sonication geometry. The dissolution process was accompanied by the progressive appearance of purple color, which was attributed to minor corrosion of the sonicating probe in the indicated acids with the formation of Ti^{3+} in the solution. Titanium(III) is a powerful reducing agent with a formal electrochemical potential of the Ti(IV)/Ti(III) couple in acidic medium close to 0 V. We hypothesized that the presence of Ti^{3+} in this system may, at least in part, be responsible for the enhanced dissolution of PuO_2. In the presence of Ti^{3+}, PuO_2 dissolution might be facilitated by reducing Pu(IV) on the surface of PuO_2 to trivalent Pu [the similar effect is known for enhanced dissolution of Fe_2O_3 in the presence of ascorbic acid, which reduces Fe(III) to Fe(II) (Banwart et al. 1989)].

In this project, we tested the addition of Ti^{3+} solution to the sonicated samples of high-fired PuO_2. The $TiCl_3$ stock solution available for use in these experiments was 10% $TiCl_3$ in 20 to 30% HCl. For this reason, we decided to perform the digestion in HCl rather than in the H_2SO_4 or H_3PO_4 media. The results of this reductive dissolution series are shown in Figure 3.1. The dissolution efficiency achieved for these conditions did not exceed 40%, which is 2.5 times lower than the previously reported values in H_2SO_4 and H_3PO_4 solutions in which Ti^{3+} generated *in situ* led to complete dissolution after 60 min of sonication. The lower efficiency of PuO_2 dissolution in this project might be associated with the lower temperature of digestion (84^oC after 60 min of digestion vs. $\sim 100^o$C after 5 to 10 min of sonication in experiments with a dip probe setup). Or, it could simply reflect the greater difficulty in dissolving high-fired PuO_2. No control series was performed with the addition of $TiCl_3$ because of an insufficiently high dissolution yield observed in the sonication run.

Figure 3.1. Dissolution Efficiency of PuO_2 in Hydrochloric Solution of $TiCl_3$. $C_{HCl} = 25\%$.

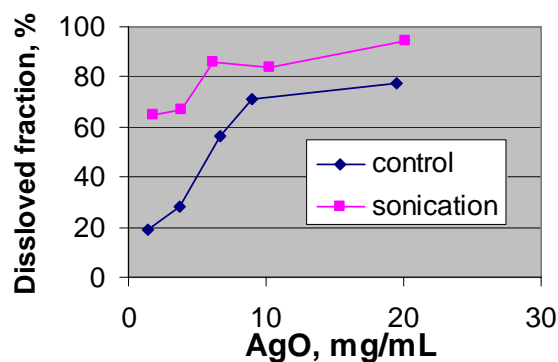## 3.5 PuO_2 Dissolution in the Presence of AgO in 1.5 M HNO_3

The Catalyzed Electrolytic Plutonium Oxide Dissolution (CEPOD) process was developed by Ryan and Bray 3 decades ago (Ryan and Bray 1980; Ryan et al. 1992) and was successfully tested for dissolution of refractory PuO_2. The process is based on the oxidative action of the Ag^{2+}/Ag^+ electrochemical couple ($E^0 = 1.98$ V). Silver(I) ions carry electrons from a solid PuO_2 surface to the anode of the electrochemical cell where the regeneration of Ag^{2+} takes place. Among other oxidizing metal species potentially suitable for oxidative dissolution of PuO_2, including Ce^{4+} and Co^{3+}, the Ag^{2+}/Ag^+ couple has by far the highest rate of electron exchange (about 10,000 times higher than those of Co and Ce), which makes it especially suitable for the CEPOD technology. In this project, we had no access to the CEPOD type of electrochemical cell that would fit inside of a sonicating cup horn cavity.

(a) GJ Lumetta, SI Sinkov, and JI Friese. 2005. *Enhancing Actinide Separations by Sonochemistry* (FY 2005 Report, Unpublished Manuscript).
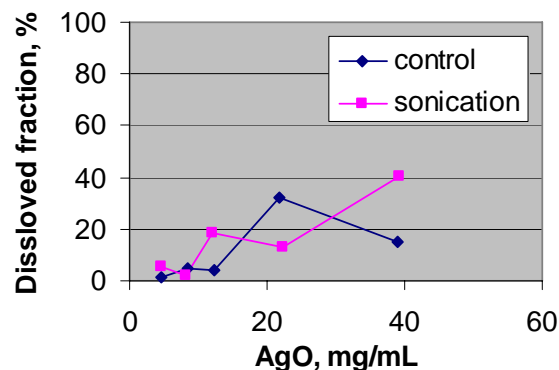
Nevertheless, we decided to test the sonochemical digestion of PuO_2 in the presence of Ag^{2+} ions introduced into the tested solution by dissolving AgO in nitric acid immediately before performing the digestion. The experiment was performed at a constant acidity of 1.4 M HNO_3 with increasing amounts of AgO powder. The results shown in Figure 3.2 indicate that about 85% of PuO_2 can be dissolved with an initial AgO concentration of 6 mg/mL under sonication. On the other hand, only 58% of the PuO_2 dissolved under these conditions in the control experiment in the absence of ultrasound. However, for higher loadings of AgO, the effect of ultrasonic treatment becomes less significant. For example, only a 15% improvement in the dissolution efficiency is achieved by sonication when the initial AgO concentration is 20 mg/mL. Incomplete dissolution of PuO_2 by this treatment might be related to the limited lifetime of Ag^{2+} in the solution because of its reduction by water with the release of oxygen ($4Ag^{2+} + 2H_2O = O_2 + 4H^+ + 4Ag^+$). Application of the CEPOD technology with Ag^{2+} regeneration is expected to improve the dissolution capability of PuO_2 in nitric acid at much lower concentrations of silver ions in the dissolving medium.

One more set of experiments on PuO_2 dissolution using AgO was performed at the same acidity but in the presence of significant amounts of Columbia River Sediment (CRS) available from the National Institute of Standards and Technology (NIST) as the Standard Reference Material (SRM) #4350B (NIST 1981). The purpose of this experiment was to determine to what extent natural organic matter (NOM) and other reducing species present in the CRS decreases the effectiveness of AgO in promoting PuO_2 dissolution. As Figure 3.3 shows, the effect of natural reducing components is very significant. It illustrates that even with twice the initial concentration of AgO in the solution than the highest loading used in the previous experiment, no more than 40% of PuO_2 can be dissolved by this treatment. The data are too scattered to allow any meaningful judgment about the benefits of sonication in this series of experiments. No information was available on the percentage of NOM in the SRM sample tested, so it was not possible to estimate whether the amount of Ag^{2+} was sufficient to dissolve all the NOM and Pu in these tests. We believe that much better results on PuO_2 dissolution in natural samples with significant amounts of NOM and other reductants can be achieved using the CEPOD-based treatment in which Ag^{2+} is electrochemically regenerated.

Figure 3.2. Dissolution Efficiency of PuO_2 in 1.4 M HNO_3 in the Presence of AgO

Figure 3.3. Dissolution Efficiency of PuO_2 Premixed with CRS (29 μg of PuO_2 per 50 ± 1 mg of the CRS) in 1.4 M HNO_3 in the Presence of AgO

3.6   PuO$_2$ Dissolution in HF

Fluoride is frequently added to nitric acid to improve the dissolution of plutonium oxides. In nitric acid solution, the concentration of the free fluoride ion might be significantly suppressed by the presence of a high concentration of protons shifting the equilibrium to favor HF formation ($H^+ + F^- = HF$, $pK_a = 3.1$). Therefore, it was of interest to compare the action of fluoride in the PuO$_2$ dissolution process as a function of free proton concentration (or more correctly, hydronium ion concentration). The lower proton concentration case was studied by applying HF alone without the presence of HNO$_3$. Figure 3.4 presents the results of the treatment with HF. The data suggest a very minor dependence of PuO$_2$ dissolution efficiency on the HF concentration under sonication, with slighter better results for higher HF concentrations. The control experiment data are very scattered, perhaps because of poor mixing during sampling or occasional penetration of a submicron fraction of unreacted PuO$_2$ into filtrates at the filtration stage. Overall, there is no indication that sonication offers any benefits in dissolution efficiency of PuO$_2$ compared with the conventional treatment. Complete dissolution of PuO$_2$ was not achieved in the HF concentration range tested, and there was no advantage in HF concentrations higher than 6 M in dissolving PuO$_2$ under sonication.

3.7   PuO$_2$ Dissolution in Mixtures of HF and HNO$_3$

In an attempt to improve the dissolution yield of PuO$_2$ in HF solution, we performed two more series of experiments in which nitric acid was added to the HF solution. In the first series, we maintained the nitric acid concentration constant at 8 M and varied the HF concentration from 1.4 to 7 M. Figure 3.5 presents the results of this experiment. Despite the presence of the strong acid—which suppresses the free fluoride ion concentration—the addition of 8 M HNO$_3$ to 2.8 M HF resulted in an 18% improvement in the PuO$_2$ dissolution efficiency for the samples not sonicated (i.e., the control experiments) and an 18% improvement in the sonicated samples. At 5.6 M HF, modest improvement was observed as well (2% and 8% for control and sonication experiments, respectively). The highest dissolution of PuO$_2$ in the HF+HNO$_3$ series was 98%, which was observed for 4.2 M HF/8 M HNO$_3$ with sonication. The control series curve also exhibits maximum dissolution at this concentration of HF (94%). The dissolution efficiency decreases by ca. 8% when nitric and hydrofluoric acid concentrations become comparable to each other (see the last two pairs of data points in Figure 3.5). It appears that a sufficiently strong concentration of free protons supplied by nitric acid is needed in addition to the presence of substantial concentrations of the fluoride containing species (HF +F$^-$) to achieve dissolution yields of PuO$_2$ higher than 95%. In addition to contributing high acidity, nitric acid also
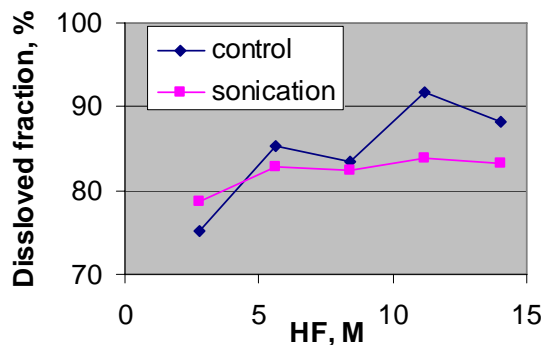
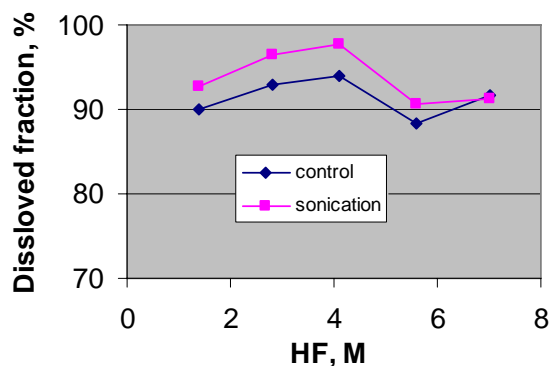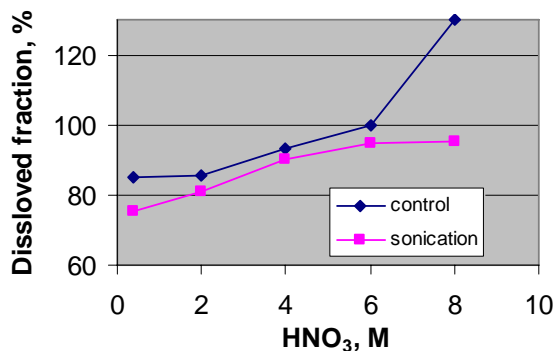**Figure 3.4.**   Dissolution Efficiency of PuO$_2$ in Hydrofluoric Acid

Figure 3.5.   Dissolution Efficiency of PuO$_2$ in HF Solution in 8 M HNO$_3$

3.4

serves as a nitrate-supplying agent that might participate in the formation of mixed fluoro-nitrato complexes of Pu(IV).

The second series of HF/HNO$_3$ experiments was performed at a constant HF concentration of 14 M with the HNO$_3$ concentration varied from 0.4 M to 8 M. Figure 3.6 shows the results of this experiment. In this case, a low HNO$_3$ concentration in the sonication series results in a minor suppression of the dissolution yield of PuO$_2$ (75% and 81% at 0.4 M and 2.0 M HNO$_3$, respectively, versus 83% observed in the absence of HNO$_3$ [Figure 3.4]). But increasing [HNO$_3$] further promotes the additional dissolution of PuO$_2$, and starting from 6 M HNO$_3$, the dissolution yield approaches 95%. It appears that both the 4:8 = 1:2 and 14:7 = 2:1 molar concentration ratios of HF to HNO$_3$ are equally effective in terms of achieving practically quantitative dissolution of plutonium dioxide in the double mixture of these acids. Contrary to the previous series of experiments, all control samples show a very minor but systematically higher dissolution efficiency than the sonicated samples. The 130% dissolution efficiency measured for the last control sample is obviously an artifact most likely related to insufficient mixing of the sample during sampling

Figure 3.6. Dissolution Efficiency of PuO$_2$ in HNO$_3$ Solution in 14 M HF

4.0 Conclusions and Recommendations

The major findings of this work can be summarized as follows:

- High-fired PuO_2 does not undergo measurable dissolution when sonicated in nitric acid solutions, even at a high concentration range of HNO_3 where the calculated thermodynamic solubility of PuO_2 exceeds the $\mu g/mL$ level (Ryan and Bray 1980).

- The application of certain organic complexants (NTA) and reductants (HU) in 1.5 M HNO_3 does not significantly increase the dissolution compared with digestion in nitric acid alone. Nearly all (99.5%) of the PuO_2 remains undissolved under these conditions.

- The action of a strong inorganic reductant, $TiCl_3$ in 25% HCl, results in 40% dissolution of the PuO_2 when the $TiCl_3$ concentration is $\geq 1\%$ under sonication.

- The oxidative treatment of PuO_2 by freshly dissolved AgO ($\sim$ 20 mg/mL) in 1.5 M HNO_3 resulted in 95% PuO_2 dissolution. However, the same treatment of PuO_2 mechanically mixed with 50 mg of CRS results in a significant decrease of dissolution yield of PuO_2 (<20% dissolved at the same AgO loading), likely because of parasitic consumption of Ag^{2+} by oxidizable components of the CRS.

- The digestion of PuO_2 in HF resulted in dissolution yields slightly higher than 80% for HF concentration from 6 M to 14 M. Sonication did not result in any improvement in dissolution efficiency in HF.

- Mixed nitric acid/HF solutions result in a higher dissolution yield of PuO_2 compared with digestion in HF alone (at the same HF concentrations). Practically quantitative dissolution of PuO_2 can be achieved with 6 to 8 M HNO_3 + 14 M HF or 8 M HNO_3 + 4 M HF mixtures. In the latter case, quantitative dissolution of PuO_2 was demonstrated only with sonication.

Overall, the results indicate that applying ultrasound in an isolated cup horn configuration for the dissolution of refractory PuO_2 does not offer any substantial advantage over the conventional "heat and mix" treatment. Oxidative treatment by AgO appears to be effective only when very little or no oxidizable materials are present in the digested sample. The catalytic use of Ag^{2+} in the CEPOD technology would probably be more effective than using AgO because the Ag^{2+} is continually regenerated electrochemically. Reductive treatment with $TiCl_3$ in an HCl medium proves to be less efficient than the previously explored effect based on *in situ* generation of Ti^{3+} in H_3PO_4 and H_2SO_4 media using a dip probe sonication geometry. The previous experiments, however, were performed at higher temperature and with non-steady concentration profiles of Ti^{3+} in the process of sonochemical digestion.

5.0 References

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