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In Vitro Dissolution Tests of Plutonium and Americium Containing Contamination Originating from ZPRR Fuel Plates

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ABSTRACT

Assessing the extent of internal dose is of concern whenever workers are exposed to airborne radionuclides or other contaminants. Internal dose determinations depend upon a reasonable estimate of the expected biological half-life of the contaminants in the respiratory tract. One issue with refractory elements is determining the dissolution rate of the element. Actinides such as plutonium (Pu) and Americium (Am) tend to be very refractory and can have biological half-lives of tens of years. In the event of an exposure, the dissolution rates of the radionuclides of interest needs to be assessed in order to assign the proper internal dose estimates. During the November 2011 incident at the Idaho National Laboratory (INL) involving a ZPPR fuel plate, air filters in a constant air monitor (CAM) and a giraffe filter apparatus captured airborne particulate matter. These filters were used in dissolution rate experiments to determine the apparent dissolution half-life of Pu and Am in simulated biological fluids. This report describes these experiments and the results. The dissolution rates were found to follow a three term exponential decay equation. Differences were noted depending upon the nature of the biological fluid simulant. Overall, greater than 95% of the Pu and 93% of the Am were in a very slow dissolving component with dissolution half-lives of over 10 years.

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In Vitro Dissolution Tests of Plutonium and Americium Containing Contamination Originating From ZPPR Fuel Plates

1. INTRODUCTION

Internal metal contamination due to inhalation is of interest to many industries, including the nuclear industry. The issues in the nuclear industry may be due to the long term health effects that are chemical in origin, but most likely will be the result of the radiological dose, particularly in the case of alpha emitters. Determining internal contamination and estimating dose is a difficult task for inhaled alpha, or beta, contamination since there is no real way to determine the amount of the radionuclide actually inhaled. An added difficulty in estimating the radiological dose is determination of the biological half-life of the radionuclide. It is difficult to know the exact chemical form of the isotope and hence the chemical and biological mechanisms that might be at work to get a radionuclide out of the body must be based on biological models. Elimination mechanisms for larger particles can include physical means such as coughing or being carried in mucous, but smaller particles are likely to reach deeper into the lung alveolar sacs and will only be eliminated by phagocytosis or dissolution into the fluids of the lung and subsequent transfer to the blood or lymphatic system for final elimination in the feces or urine.

ICRP Publication 66[3] describes the methods for determining the dose via a respiratory tract model that uses default values for the absorption of radionuclides into the blood based upon whether the absorption is fast, medium or slow (F, M, or S). The ICRP consistently recommends that, when possible, material specific absorption parameter values be used that are determined from *in vivo* data. However, since *in vivo* data is difficult to come by, material-specific *in vitro* experimental data can and should be used[2]. In general, the results for this model express the undissolved fraction in the lungs as

$$f_r = f_f e^{-k_r t} + f_s e^{-k_s t} \tag{1}$$

where:

f_r = the remaining fraction at time t

f_f = rapid dissolving fraction

f_s = slow dissolving fraction

k_r = rapid dissolution rate

k_s = slow dissolution rate

$f_f + f_s = 1$.

A November 2011 incident at the INL resulted in several individuals being exposed to airborne Pu contamination from degraded Pu fuel plates from ZPPR. The airborne contamination was due to PuO_2 which also carried the decay products of Am and significant U because the fuel plates are ~2/3 by weight U. While these other elements may be present, Pu is the element with the radioisotopes of major concern in this incident. The ICRP Publication 66 defines the variables for Pu in the above equation as follows in Table 1.

Using the relationship that $k_x = 0.693/t_{1/2}$ and the values from this table, it can readily be seen that the dissolution half-life of Pu ranges from ~10 minutes for soluble compounds such as nitrates to over 7000 days (19 yrs) for insoluble compounds like most of the oxide forms suspected by the nature of the ZPPR

Table 1. ICRP recommended values for equation 1 when Pu is of interest. [1]

Pu Compound Dissolution Type	ff	Kf (d-1)	fs	Ks (d-1)
Rapid	1	100		
Medium	0.1	100	0.9	0.005
Slow	0.001	100	0.999	0.0001

fuel plates. One should note that dissolution rates can also be affected by the initial particle size and shape which affect the surface area and may change with time as the particles become smaller increase in surface area. So, not only the nature of the compound containing the radioisotope but also the particle size and shape can combine with various biological processes (phagocytosis) to dramatically change the rates of absorption and elimination. The evidence for this is supported by the wide range of parameters for Eq. 1 found in a variety of *in vitro* and *in vivo* studies of many Pu containing materials.[1] The net conclusion of Davesne, et. al. is that the ICRP provides a reasonable approximation of the absorption parameters assuming that PuO_2, MOX, oxide graphite, Maralinga soil and Palomares dust are insoluble (Type S) while Pu nitrates, Pu chlorides, Pu-Na alloy, Pu-Mg alloy, Pu-TBP complex and other industrial residues are moderately soluble (Type M) and Pu citrate is soluble (Type F).

There does not appear to be a standardized method for doing a material-specific *in vitro* dissolution study as many methods have been published using a variety of lung fluid simulants and test configurations.[4-8] Some have even used macrophage phagolysosomal fluids which trend away from neutral pH to pH near 4.5.[8, 9] In 1999, Ansoborlo et.al.[2] reviewed *in vitro* dissolution methods and recommended two simultaneous tests with two different solvents. The recommended solvents were the serum ultra filtrate fluid (SUF) and a culture medium such as 199 Gibco. This latter fluid is a rather complex growth medium that is not representative of lung fluid. Therefore, for lung fluid simulants, serum ultra filtrate (SUF)[2, 8, 10], simulated lung fluid (SLF)[2, 7] or Gambles's solution[2, 4, 6] are most common (see Table 2). Gamble's solution and SLF are relatively simple solutions with a pH 7.2-7.4 and can be assumed to mimic biological fluids after removal of large protein molecules. The SUF is similar; however, it contains diethyenetriaminepentaactic acid (DTPA) and alkylbenzyldimethyl ammonium chloride (ABDC). The compound DTPA is a chelating agent used as a therapeutic detoxification "drug" for internal metal contamination cases and is not otherwise found in biological fluids. The function of DTPA here is mainly to prevent precipitation of the elements of interest as phosphates but it may also act to enhance solubility of some elements. The compound ABDC is used primarily as an antimicrobial agent since the dissolution tests can be quite lengthy, giving rise to the possibility of microbial growth that may influence the results.

Available samples from the INL Pu fuel plate incident were limited. Initially, nasal swabs were used to assess the contamination in the nostrils of the affected individuals. These samples were consumed for isotope specific analysis by alpha spectroscopy for Pu, Am and U isotopes. The maximum total activity for any swab was ~211 pCi (7.82 Bq) which can be broken down to 128 pCi, 7.2 pCi, and 86.2 pCi for $^{239+240}$Pu, ^{238}Pu, and ^{241}Am, respectively. Additional samples were also acquired during or after the incident and included smears and air filters from a CAM and a Giraffe sampling apparatus. These samples were analyzed by gamma spectroscopy but only ^{241}Am was found as expected since the other isotopes are alpha or pure beta emitters. Using the last assay data for the Pu plates in 1983 and decaying forward to 2011, the ratios of $^{239+240}$Pu/^{241}Am and ^{238}Pu/^{241}Am should be 1.62 and 0.15, respectively. The nasal swab data had $^{239+240}$Pu/^{241}Am and ^{238}Pu/^{241}Am ratios of 1.67±0.20 and 0.10±0.02, respectively. Since the calculated and experimentally determined ratios were in reasonable agreement, it is possible to estimate the concentrations of the various radioisotopes that could be on the smears and filters using the 1983 assay decayed to 2011 and the ^{241}Am analysis data for each sample. The results are in Table 3.

Table 2. Compositions of biological fluid stimulants.[2]

Salt	**Molar Concentrations** **SUF**	**SLF**	**Gamble**
KCl		0.004	
NaCl	0.116	0.145	0.116
MgCl2		0.001	
NH4Cl	0.010		0.01
NaHCO3	0.027	0.024	0.027
Glycine	0.005		0.006
L-Cysteine	0.001		0.001
Na3Citrate	0.0002	0.0003	0.0002
NaActetate		0.007	
CaCl2	0.0002	0.0025	0.0002
H2SO4	0.0005	0.0005	
Na2SO4		0.002	
Na2HPO4			
NaH2PO4	0.0012		0.0012
DTPA	0.0002		
ABDC	50 ppm		

Table 3. Estimated concentrations for various radioisotopes on smears and filters based on the decayed 1983 assay values and the actual recent ^{241}Am of the samples as determined by gamma spectroscopy.

MFC Sample number	94423	94424	94425	94422	94418
Sample ID	Smear 17 (nCi)	Smear 24 (nCi)	Smear 23 (nCi)	CAM Filter (nCi)	Giraffe Filter (nCi)
Pu238	0.059	0.121	0.071	0.063	0.350
Pu239	0.430	0.886	0.521	0.461	2.568
Pu240	0.209	0.430	0.253	0.224	1.246
Pu241	2.525	5.203	3.062	2.710	15.086
Pu242	6.E-05	1.E-04	7.E-05	6.E-05	4.E-04
U234	5.E-06	1.E-05	6.E-06	6.E-06	3.E-05
U235	1.E-07	2.E-07	1.E-07	1.E-07	6.E-07
U238	7.E-06	1.E-05	8.E-06	7.E-06	4.E-05
Am241	0.395	0.814	0.479	0.424	2.360
Total	3.617	7.454	4.386	3.883	21.611

The air filter samples were preferred for total radioisotope analysis to provide contamination data and to estimate the potentially inhaled dose. The smears likely do not have evenly distributed particles and are more difficult to use in the dissolution studies. It was, however, reasonable to assume that the collected particulate on the CAM and Giraffe filters was evenly distributed. Therefore division of these filters to provide sample replicates was much more likely to result in sections with equal activities.

2. EXPERIMENTAL

Two simulant fluids were prepared using the recipes from Table 2. The selected fluid simulants were the SUF and Gamble solution. The SUF was selected as it is similar to the other fluids but also contains DTPA which would possibly simulate individuals treated with DTPA or may represent more complex molecules in the body capable of chelation. The Gamble solution was selected as it has commonly been used for such studies for decades.

One section of each filter sample (1/4 of the sample) was immediately submitted for full analysis of Pu and Am isotopes to verify the original estimates of activity and to allow calculated estimates of potential inhaled dose. This also allowed ongoing assessment of dissolution rates until the fraction remaining of each sample can be determined at the end of the tests.

Only the CAM and Giraffe filters listed in Table 3 were used for this study. Each filter was weighed dry, cut in to 4 equal sections and each section weighed. These masses were used to estimate the activity on each section of each sample using the data in Table 4. One section of each filter was saved as an archive, two sections were used in the actual experiment with the two different simulant solutions and the fourth saved for further analyses.

Table 4. Table 3 activities adjusted to show the estimated amount of material used in each experiment in terms of activity and mass.

Sample ID	CAM Filter (nCi)	CAM Filter (ng)	Giraffe Filter (nCi)	Giraffe Filter (ng)
Pu238	0.016	0.001	0.088	0.005
Pu239	0.115	1.857	0.642	10.338
Pu240	0.056	0.247	0.311	1.372
Pu241	0.678	0.007	3.772	0.037
Pu242	1.6E-05	0.004	9.0E-05	0.023
U234	1.4E-06	2.3E-05	7.9E-06	1.3E-04
U235	2.8E-08	0.013	1.6E-07	0.073
U238	1.8E-06	5.258	9.8E-06	29.269
Am241	0.106	0.031	0.590	0.172
Total	0.971	7.418	21.611	165.153

The actual lung dissolution tests were performed using the static sandwich filter method[1, 2, 4-10] with the two sections of each sample. Holders for the sandwich filters were made of Teflon® and the two halves were made to fit together snuggly to hold the filter sandwich in place. A section of each sample was placed between two membrane filters with a pore size of 100 nm (Millipore Durapore WPP). The assembled filter sandwich apparatus was submerged in 100 mL of a simulant fluid in an ICHEM jar (see Figure 1) maintained at a constant temperature of 37°C on a hot plate in an air atmosphere. A needle was pierced through the lid of the ICHEM jar to allow exchange with air and to prevent any pressure buildup. The only mixing was via convection from the temperature gradient created by the hot plate surface and air temperature. The pH was maintained in the range of 7.2-7.5.

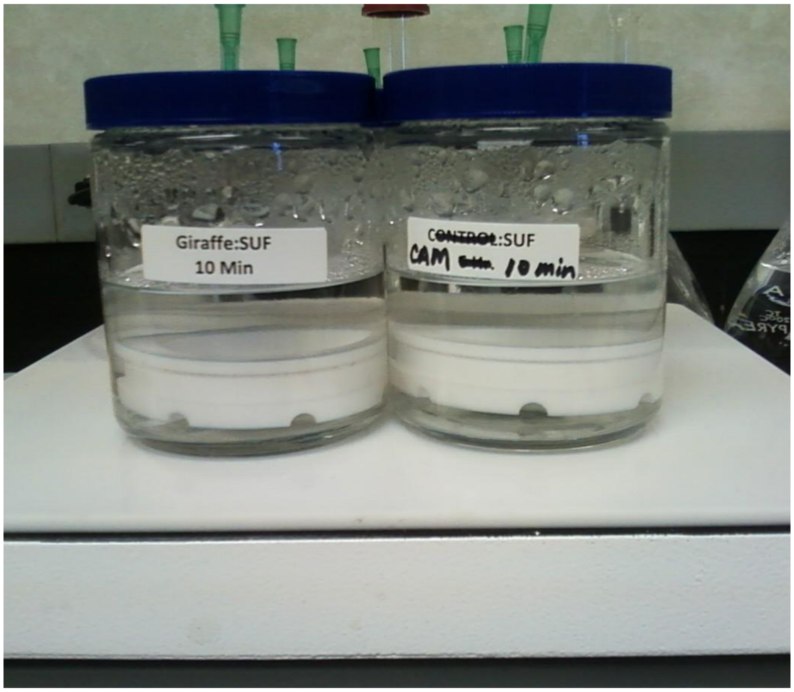


Figure 1. Filter sandwiches submerged in 100 mL of simulant.

At specified time intervals sufficient to determine a half life on the order of minutes to hours and then thousands of hours, the simulant solution of each filter sandwich was replaced with fresh simulant solution of the same type. For this work, the sampling schedule was modeled after that of Dias da Cunha et. al.[4] with sampling times of every 10 minutes for the first hour then at 2, 4, 6, 8 and 24 hrs then daily for 1 week, weekly through the first month, and then monthly to 3 months. After the leachates were collected they were acidified with HNO_3 and divided into three parts. Half (50 mL) was used for total isotopic analysis by decomposition (necessary due to the DTPA chelating agent), preconcentration, separation, precipitation and alpha spectroscopy using standard procedures at the Radioanalytical Chemistry Laboratory (RaCL). Of the remaining 50 mL, 30 mL was saved as an archive and the remaining 20 mL was used for screening by liquid scintillation counting (LSC) and inductively coupled plasma mass spectrometry (ICPMS). Analysis by LSC had promise because as can be seen in Table 3, the majority of the total activity on the filter samples is due to ^{241}Pu, a pure β emitter. Table 4 indicates that some of samples may have also had sufficient mass for ICPMS screening of the dissolved fractions as the detection limits by ICPMS in the mass range of 230-245 are typically less than 1 pg/mL. Unfortunately, neither LSC or ICPMS proved useful as a screening tool since the maximum concentration in the solutions analyzed were less than the detection limit and will not be discussed further.

Concern about DTPA, ABDC, citrate, amino acids and/or microbial growth affecting the column separations for the Pu and Am were alleviated by complete dissolution of the the sample fractions used for alpha spectroscopy. This was of particular concern for the Gamble solution which appeared to have a white suspension after several days suspected to be due to microbial growth. Briefly, the analysis procedure consisted of evaporating 50 mL of each simulant solution to near dryness then digesting with a nitric/sulfuric acid combination over heat. The samples were spiked with ^{243}Am and ^{242}Pu as tracer/isotope dilution standards. These digests were then transferred to beakers in 2.0 N HNO_3. Valence state adjustments were made using ascorbic acid and sodium nitrite, and then the samples were loaded onto a TEVA column stacked on top of a TRU column (Eichrom). The loaded column stack was then rinsed with 4.0 N HNO_3. Once separated the TEVA column was eluted with 6 N HCl to assure no interference from Th isotopes. The Pu was then eluted with a solution of $TiCl_3$ and 0.5 N HCl. Americium was recovered from the TRU column with 4.0 N HCl. The eluted sample fractions were then co-precipitated with NdF_3 after the addition of 100 µg Nd followed by the addition of 5 mL of concentrated HF. The precipitates were collected on 0.1 µm polypropylene filters. The filters were dried under heat and vacuum then counted for 20 hours by alpha spectrometry.

Total analysis of the filter sandwich was performed at the end of 90 days. The filter sandwich was removed from the Teflon holder and placed in an Erlenmeyer flask with a powder funnel inserted in the top and placed on a stirring hotplate. The Durapore filters and the Teflon filter sections that were the CAM and Giraffe filters were continuously leached and refluxed in hot 2$\underline{M}$ HNO_3 and agitated for 7 days to assure the maximum dissolution and dislodgment of particles on the filter surfaces. To assure all particles removed were completely dissolved, the leachates were evaporated to dryness in platinum crucibles and fused using sodium metaborate at 1000°C. The fused sample cakes were dissolved in ~2 $\underline{M}$ HNO_3 and analysis proceeded through separation and co-precipitation as described above.

Data analysis to solve the exponential decay equations was performed using the built-in algorithms in SigmaPlot (ver. 11.2.0.5) which are based upon the Marquardt-Levenberg algorithm. Critical to the implementation of this algorithm to solve the equation(s) was to confine the solution such that the sum of the fractional terms in the equation equal 1, i.e. $f_1 + f_2 + ... + f_n = 1$. This was done in the study reported here, which is an improvement over that of the Gel Laboratory study.[10] Failure to do so in that study resulted in the nonsensical conclusion that $f_f + f_s = 1.33$ for Pu and 1.61 for Am in one of the two samples tested. Because of the long half-lives relative to the time of the experiment, no decay corrections were made as the expected differences were 1% or less which is well within the actual experimental and analytical errors which range as high as 10% or more.

3. RESULTS AND DISCUSSION

A criticism of nearly all of the dissolution studies that have been performed on refractory element/compounds is that there are not sufficient data points to adequately determine the coefficients for Eq. 1. There are often too few points to determine the fast dissolution component, particularly if ICRP is correct and the dissolution half-life of that component is on the order of 10 minutes. In addition, if the slow component half-life is on the order of 7000 days (i.e. 19+ yrs), then stopping the test at 1, 2, 3 or 6 months is likely to be far too short for many very refractory elements and compounds. These types of studies are properly conducted over 6-12 months, or more, when the dissolution rates are quite slow as is the case for Pu. In general, this study supports that criticism.

The data in Table 4 are estimates of the expected total activity on the quarter filter sections used in the experiment. Table 5 lists the total activity actually observed on each section plus a third section that had originally been designated for total analysis. It was anticipated that the activity on the CAM and Giraffe air filter samples would be much more evenly distributed than that of the smears. The data in Table 5 disputes that assumption. Without knowing what the particle count and particle size distribution of the filter sections actually was, there is no way to conclusively state why the mean total activities vary by 20% to 50% on these filters. The reason is most likely due to the number of large particles on each section. Two of the CAM and two of the Giraffe filter section results are in reasonable agreement with each other and the aniticpated values in Table 4. One CAM and one Giraffe section were significantly higher than expected. Even the actual concentrations did vary somewhat from the original estimates, the fact that very little material actually leached from the samples over the 90 days of the experiment made little difference to the on-going estimates of the dissolution parameters during the course of the experiment.

There are many factors which can affect the dissolution rate of an element from a particular matrix including such things as the chemical form(s) containing the element of interest, the particle size distribution, and the overall heterogeneity of the matrix. Because of these and other factors, the dissolution over time will show multiple rates depending on the primary factors influencing that rate at any given point in time. Examination of the data in Figures 2 and 3 clearly supports this concept since it is easy to note that at least a three term exponential decay equation is necessary to describe the observed dissolution behavior. One term describes a very fast dissolving component during the first few hours, a second term describes a component that dissolved more slowly over the following several days and a third term describes a refractory component that dissolved only slowly after 30-60 days. To describe this behavior requires the addition of a third term to Eq. 1 as

$$f_r = f_f e^{-k_f t} + f_m e^{-k_m t} + f_s e^{-k_s t} \tag{2}$$

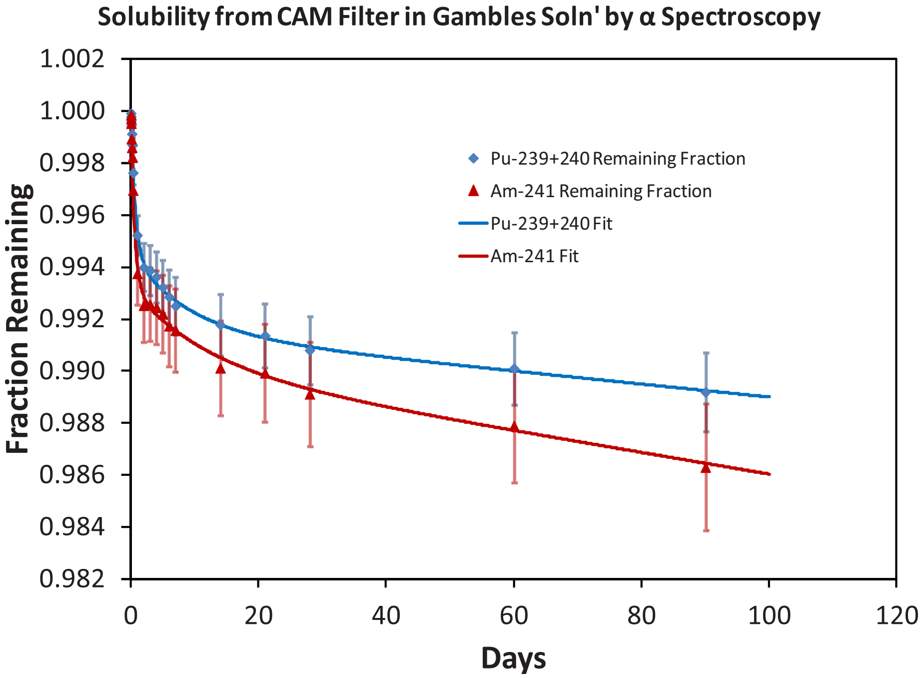
where f_f, f_m, and f_s are the fast, medium and slow dissolving fractions, respectively, of the total quantity of the element of interest that is present initially, f_r is the remaining fraction at time t and k_f, k_m, and k_s are the fast, medium and slow dissolution rate constants, respectively. Table 5 shows the constants determined for Eq. 2 in the four separate experiments and the fit lines in Figures 2 and 3 were calculated using these coefficients.

Differences between the filter sections in Gamble and SUF are readily apparent. Overall, the SUF appears to enhance the dissolution of the fast and medium dissolution rate components but appears to have a much smaller to negligible effect on the slow dissolving components. This is most likely due to the DTPA enhancing the solubility of some materials, at least to some degree.

The fast dissolving component fraction (f_f) was less than 1% of the total for both Pu and Am in the Gamble solution. In the SUF, the fast dissolving fraction of Pu and Am was in the range of 1% to 2+%. Similarly, the component fraction (f_m) with the moderate dissolution rates (k_m) were <<1% in the Gamble solution and up to 5% in the SUF. The f_m for Am in the SUF experiments is nearly two times the Pu fraction indicating somewhat enhanced solubility of Am, at least in the moderate dissolution fraction. The k_m is much smaller in the SUF than in the Gamble solution, possibly indicating the enhanced solubility of some components due to the DTPA. The dissolution rate (k_f) for the fast dissolving component is similar for both samples and simulant solutions but the moderate dissolution rates are nearly three times faster in the SUF than the Gamble solution.

It is obvious that the slow dissolving components make up the majority of the material on each of the filter sections. However, the dissolution rates (k_s) appear to be little different regardless of the filter or the simulant solution used in the experiment. Since the dissolution rate values decrease, one can speculate that if the DTPA enhances solubility at all it is for the medium dissolution rate fraction and that this is likely due to particle size distributions, i.e. dissolution of very small solid particles with very high surface area.

Careful examination of the values in Table 5 shows that the standard errors for the coefficients are often relatively large in comparison to the value of the constant. There are several reasons for this including the fact that the slow and medium dissolving fractions are really quite small relative to the total, particularly when considered together with the experimental and analytical errors. This amplifies any analytical errors, thus causing more variation in the determined coefficients. Since the experiment was terminated at 90 days due to time constraints, the lack of data beyond 90 days limits the ability to clearly define the long dissolution fraction constants. Once again the rate of dissolution relative to the experimental and analytical errors is quite small for the 30, 60, and 90 day data. For example, in the case of the Giraffe Filter in SUF, it is not clear that the dissolution curve had actually reached the final slow dissolution rate slope and estimated k_s to essentially be zero with a standard error in the 1e-4 range. Using only a single term exponential decay with the data from 30, 60 and 90 days as a basis for estimating k_s resulted in k_s estimates of 7.78e-5 for Pu and 2.2e-4 for Am. With the 60 and 90 day data estimates of k_s are 4.67e-5 and 7.68e-5 for Pu and Am, respectively.



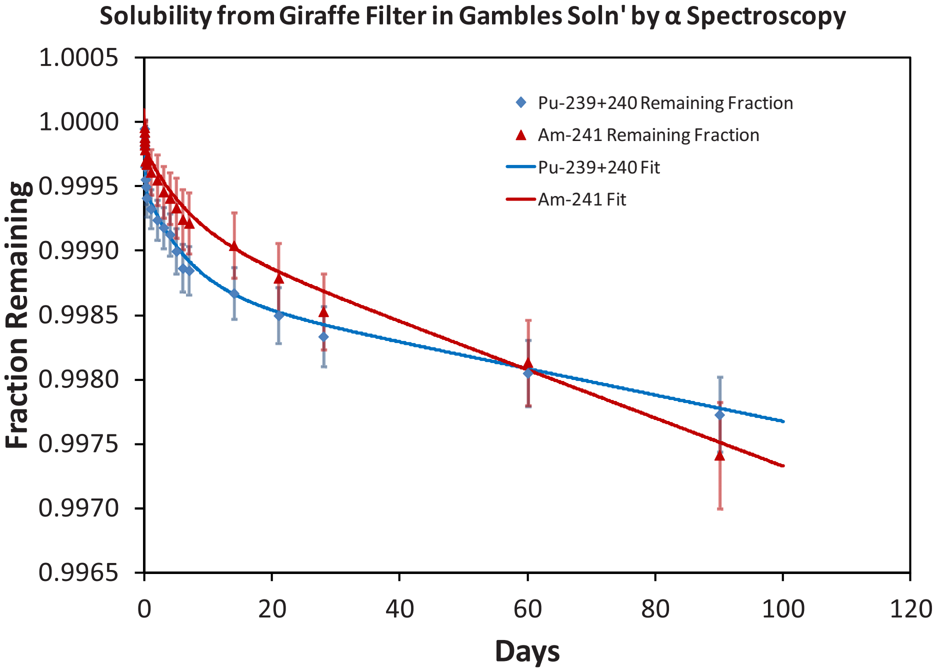


Figure 2. Dissolution of Pu and Am from the CAM and Giraffe Filters using Gamble solution.

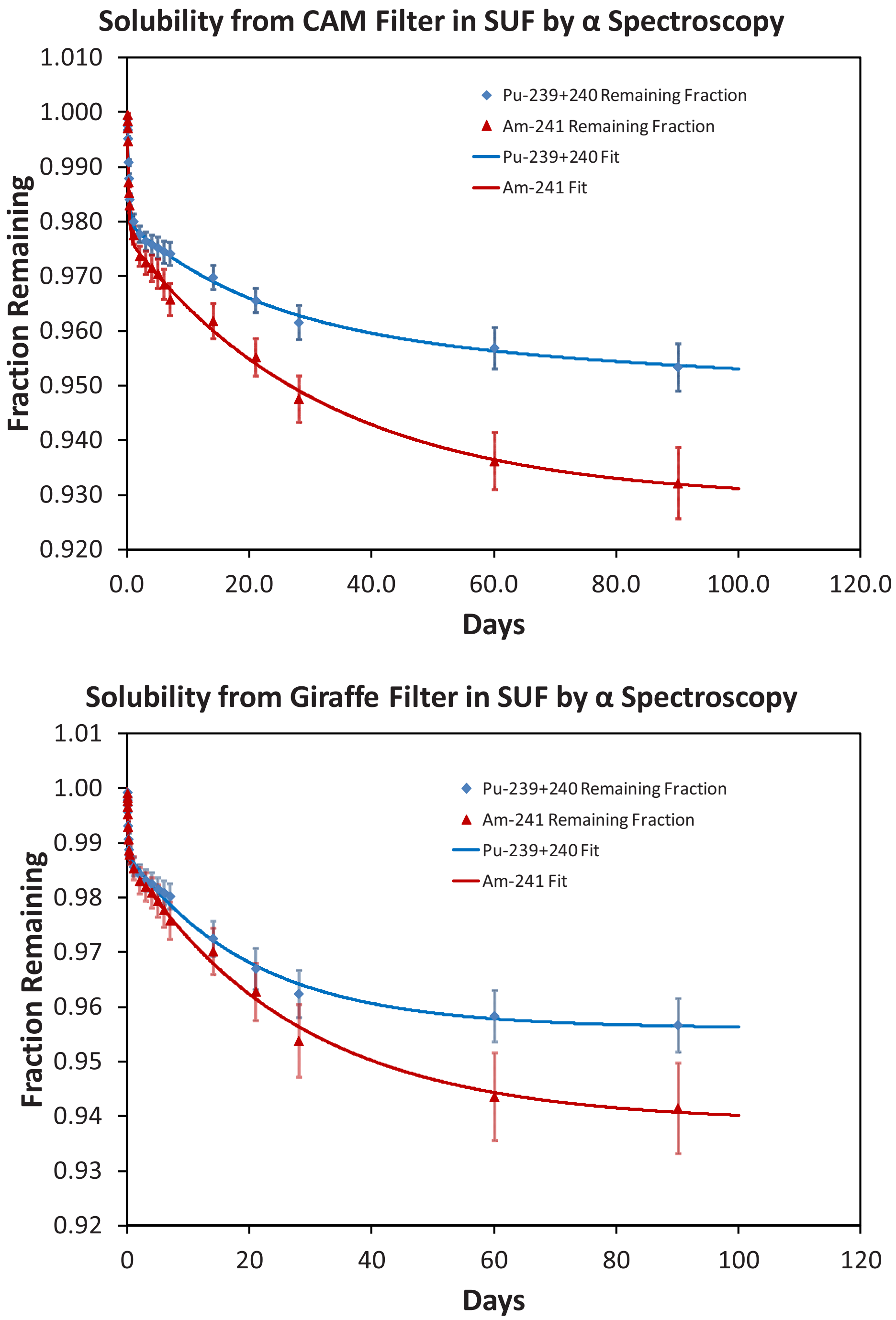


Figure 3. Dissolution of Pu and Am from the CAM and Giraffe Filters using SUF solution.

Table 5. Total analysis results of the quarter filter sections used in the experiment and a third quarter section designated for total analysis.

	$^{239+240}$Pu (pCi)	^{241}Am (pCi)
CAM Filter		
Gamble Section	194 ± 24	110 ± 18
SUF Section	78 ± 10	55 ± 9
3rd Section	103 ± 12	65 ± 9
Mean	125 ± 61	77 ± 30
Giraffe Filter		
Gamble Section	787 ± 77	490 ± 56
SUF Section	773 ± 84	618 ± 84
3rd Section	1,305 ± 144	780 ± 96
Mean	955 ± 303	629 ± 145

Turning the k_x *values* into half-lifes ($t_{1/2}$) in terms of days is shown in Table 6. Linking the data between the two tables again leads to the observation that the majority of the available activity is in the slow dissolving component and that this component has a very long half-life for dissolution. Generally the half-life for Am is somewhat less than that of Pu in the slow dissolving fraction, however, not significantly. The shortest half life for Am in the slow dissolving component was in the range of 3500 days (~9.5 yrs).

Table 6. Coefficients calculated using Eq. 2 for the material collected on the CAM and Giraffe filters and leached for 90 days in a filter sandwich.

	f_f	k_f (d^{-1})	f_m	k_m (d^{-1})	f_s	k_s (d^{-1})	R^2
CAM Filter in Gambles Solution							
Pu	0.0055 ± 0.0005	1.41 ± 0.23	0.0030 ± 0.0004	0.110 ± 0.050	0.9915 ± 0.0005	2.5E-5 ± 7.1E-6	0.9972
Am	0.0068 ± 0.0005	1.64 ± 0.25	0.0030 ± 0.0007	0.085 ± 0.055	0.9902 ± 0.0009	4.2E-5 ± 1.2E-5	0.9963
Giraffe Filter in Gambles Solution							
Pu	5.0E-4 ± 3.8E-5	10.8 ± 2.4	8.0E-4 ± 4.8E-5	0.144 ± 0.019	1.0E+0 ± 4.8E-5	1.0E-5 ± 7.7E-7	0.9976
Am	3.0E-4 ± 7.2E-5	17.6 ± 10.2	6.0E-4 ± 6.5E-5	0.139 ± 0.034	1.0E+0 ± 6.6E-5	1.9E-5 ± 1.1E-6	0.9958
CAM Filter in SUF							
Pu	0.0201 ± 0.0007	3.68 ± 0.34	0.022 ± 0.006	0.043 ± 0.014	0.9575 ± 0.0062	5.0E-5 ± 6.9E-5	0.9979
Am	0.0229 ± 0.0013	3.76 ± 0.55	0.048 ± 0.021	0.031 ± 0.013	0.9290 ± 0.0219	2.3E-25 ± 2.0E-4	0.9968
Giraffe Filter in SUF							
Pu	0.0120 ± 0.0008	8.73 ± 1.77	0.032 ± 0.005	0.049 ± 0.010	0.9561 ± 0.0056	2.1E-27 ± 6.5E-5	0.9968
Am	0.0126 ± 0.0010	8.28 ± 1.98	0.049 ± 0.012	0.036 ± 0.010	0.9389 ± 0.0128	2.1E-18 ± 1.0E-4	0.9970

The difficulty of estimating the parameters with the given data is also demonstrated in Table 6. The half-life of the slow dissolving component can only be estimated from the standard error of the estimate of k_s, since the determined value was essentially zero. This leads to an estimated half-life in the range of infinity. Using the 30, 60 and 90 day data only, the $t_{1/2}$ values can be estimated at 8900 and 3150 days for Pu and Am, respectively. With only the 60 and 90 day data, estimates of $t_{1/2}$ for Pu and Am grow to 14900 and 9000 days respectively.

According to ICRP, if the remaining fraction after 180 days is >0.87, then the material would be classed as Type S[11]. Using the 3 term exponential equation solutions from Table 5 to extrapolate to 180 days, the smallest fractions remaining at 180 days were determined to be 0.960 and 0.928 for Pu and Am, respectively. Based upon this, both Pu and Am would be classes as Type S from this experiment.

Table 7. Estimated half-lives of the fast, medium and slow dissolving components determined from k_f, k_m, and k_s as listed in Table 5.

	Half life in days		
	Fast	**Medium**	**Slow**
CAM Filter in Gambles Solution			
Pu	0.49 ± 0.08	6.28 ± 2.85	27,433 ± 7,708
Am	0.42 ± 0.06	8.12 ± 5.22	16,442 ± 4,874
Giraffe Filter in Gambles Solution			
Pu	0.06 ± 0.01	4.83 ± 0.65	67,492 ± 5,045
Am	0.04 ± 0.02	4.98 ± 1.23	36,934 ± 2,075
CAM Filter in SUF			
Pu	0.19 ± 0.02	16 ± 5	13,996 ± 19,391
Am	0.18 ± 0.03	22 ± 10	> 3,466
Giraffe Filter in SUF			
Pu	0.08 ± 0.02	14 ± 3	> 10,633
Am	0.08 ± 0.02	19 ± 5	> 6,931

[a] Estimated from standard error since the slow dissolution rate from the fit is essentially zero ± standard error since there were too few data points at the longer times. Assume that >84.6% of the estimates for $t_{1/2}$ will be greater than this number.

4. CONCLUSIONS

Even though the experiment was stopped at 90 days, there is compelling evidence to support the conclusion that both Pu and Am dissolution rates are in the Type S category. The solubility of both elements was quite slow in both of the simulant solutions used in this study. There were some differences in the solubility with that were almost certainly due to the composition of the two simulant solutions used. The solubility in the Gamble solution was very low and may have been affected by microbial growth or precipitation. Microbial growth would adversely affect the result, however, since precipitates or microbial biomass in suspension would still be sampled and analyzed by total digestion the affect should be small. The presence of ABDC and DTPA in the SUF enhanced the Pu and Am solubility, particularly of the moderate dissolution rate fraction. It appears that the slow dissolving fractions of both Am and Pu have half lives >3500 days and possibly as long as tens of thousands of days.

Dissolution rate experiments such are this are subject to many sources of error and uncertainty. Among the sources of uncertainty is the biological fluid simulant itself. The addition of ABDC and/or DTPA to the SUF prevented “clouding” up of the solution over time, but may have also altered the dissolution profile by enhancing a moderate dissolution rate component forcing a three-term exponential decay model to be required. However, it is unclear what dissolution processes and chemicals are really occurring in a live biological system. Therefore the use of the SUF may be preferable over the Gamble solution as it is easier to identify Type S and Type M solubility. However, no matter what biological simulant solution is used, the study should use no less than 6 months leaching time.

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