Lung Solubility Evaluation of Plutonium and Americium in Waste Material

Introduction

The goal of every radiation safety program is to keep exposures as low as reasonably achievable. In the United States the limits for exposure to radiological workers is 5 rem per calendar year for the whole body and 50 rem for any specific organ. These limits are based on a 50 year committed effective dose equivalent (CEDE). Quite often dosimetry calculations assume worst case conditions and assigned doses are higher than what an individual has actually received. Knowing the solubility class of a material is helpful to properly assign the internal dose following an unplanned exposure.

The purpose of this study was to evaluate the lung solubility class of plutonium and americium in waste materials related to an unplanned occupational exposure. The material from the radiological source was used to conduct this study and provide the best possible information available in combination with urine bioassay to arrive at the final determination of radiological dose. Various lung solubility methods have been developed to reproduce the process of removing foreign material from the lung. This study replicated the solubility of selected materials when subjected to simulated lung fluid (SLF) under similar conditions as found in the human lung. Specifically, SLF was placed in contact with a "filter sandwich" containing elevated levels of plutonium and americium to determine their solubility rates in lung fluid over time. The solubility rates were then compared to those in ICRP 66 for the determination of the most appropriate solubility class.

Experimental

SLF was prepared according to the composition given for serum ultra filtrate (Ansonborlo et. al. 1999) and are provided in Table 1. After the reagents were dissolved in deionized water, the solution was adjusted to pH 7.3 with H_2SO_4.

Table 1: Simulated Lung Fluid Composition

NaCl	6.779 grams per liter	Na_3Citrate	0.059 grams per liter
NH_4Cl	0.535 grams per liter	$CaCl_2$	0.029 grams per liter
$NaHCO_3$	2.268 grams per liter	NaH_2PO_4	0.166 grams per liter

Glycine	0.375 grams per liter	DTPA	0.0787 grams per liter
L-Cysteine	0.121 grams per liter	H_2SO_4	0.1 M added to adjust to pH 7.3

The original sample selected for this study was analyzed for radiochemistry parameters and the results are shown in Table 2. The matrix of the sample was a fibrous HEPA filter material. A glass fiber material was wiped within the original sample container to obtain sufficient activity for the study. The table illustrates how the original sample activity extracted into the SLF at similar percentages. This comparison suggests the plutonium and americium have similar solubility characteristics in the SLF. The activity ratios are similar in the total analysis as compared to the material extracted into the SLF. This is noteworthy since plutonium is known to form very insoluble compounds while americium is less often observed in insoluble forms.

Table 2: Comparison of original sample activity percentages with solubility data

	Original Activity, uCi/g	2 Sigma Uncertainty, uCi/g	% of original total activity	% observed in SLF
Pu-238	3.22e-1	2.38e-2	22.7%	26.9%
Pu-239/240	2.67e-1	2.17e-2	18.8%	21.3%
Am-241	8.28e-1	5.51e-2	58.4%	51.8%

GEL selected a static system approach (Ansoborlo ET. AL. 1999) in this study with two filters enclosing a third filter to form a “sandwich” that contained americium and plutonium contaminants. The outer filters were contaminant free and allowed the SLF to pass through and interact with the contaminants. 47 millimeter Millipore ™ 0.1um cellulose ester filters were chosen to enclose the contaminated filter as recommended in the static method test (Ansoborlo ET. AL. 1999). The vessels used to hold the filter sandwich and lung fluid were modified Millipore brand Sterifil® aseptic 47 mm filter holders (see Figures 1-3). Modification was required to the filter holder and included adding a plastic 47mm cover to the lower mesh opening to prevent any simulated lung fluid from leaking during the extractions. The collection portion at the bottom of the system was filled with sand to improve the vessels stability in the water bath

while not allowing the sand to come into contact with the SLF or filters. The vessels were placed in a water bath capable of maintaining the SLF at 37 degrees Celsius. A constant supply of carbon dioxide gas was purged across the surface of the SLF during extraction intervals. 100 ml of SLF was used for each extraction and daily exchanges were made for 7 days followed by weekly exchanges at 14, 21 and 28 days. The analyst noted that some evaporation occurred over time in the vessels due to the carbon dioxide flow. SLF was added to ensure the filter sandwiches would not dry and to maintain an average of 100 mls SLF. All the SLF extracts were diluted after the leaching period to 200 mls to accommodate the gamma spectrometry calibration geometry. 2 mls of sample were taken for analysis with a fraction of 0.01 sample as the adjusted aliquot. In this manner all results were adjusted back to pCi/sample for consistent reporting. At the end of the 28-day experiment, the filter sandwich was ashed and digested to determine the amount of activity remaining after 28 days. SLF extracts and the original filters were analyzed by alpha spectrometry for plutonium 238, 239/240 and americium 241 according to GEL standard operating procedure GL-RAD-A011 with results corrected to pCi/sample. Additionally americium was determined by gamma spectrometry as a cross check with the alpha spectrometry results. Curve fits and equations were based on alpha spectrometry data only.

Figure 1: Modified Millipore Sterifil® Aseptic 47 mm Filter Holders

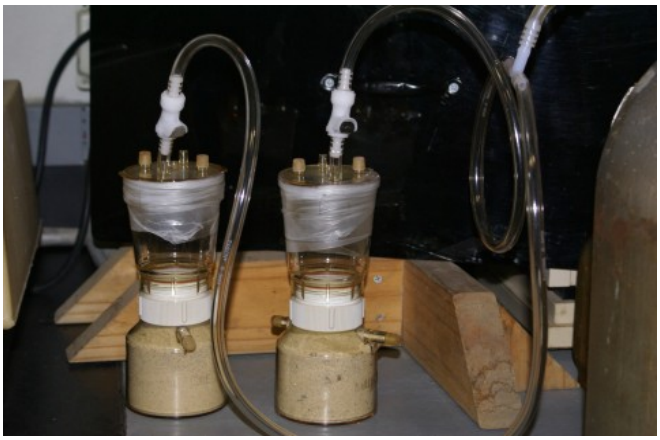


Figure 2: Simulated Lung Fluid Addition to Filter Sandwiches

Figure 3: Carbon Dioxide Gas Being Passed Over Simulated Lung Fluid and Samples

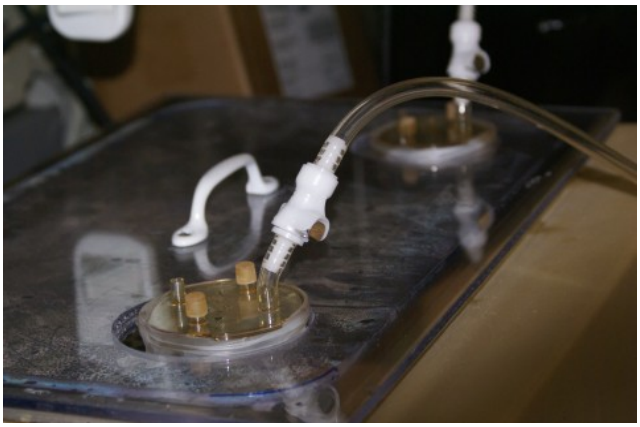


Table 3 is provided to show the Laboratory Information Management System (LIMS) assigned numbers and the dates of extraction exchanges. This information is helpful to cross reference the analysis raw data used in this study.

Table 3: Sample Data Summary

Day	Extraction Date(1)	Sample 1 LIMS ID	Sample 2 LIMS ID	Day	Extraction Date(1)	Sample 1 LIMS ID	Sample 2 LIMS ID
1	9/19/07	193883001	193883002	7	9/25/07	193883013	193883014
2	9/20/07	193883003	193883004	14	10/02/07	193883015	193883016
3	9/21/07	193883005	193883006	21	10/09/07	193883017	193883018
4	9/22/07	193883007	193883008	28	10/16/07	193883019	193883020
5	9/23/07	193883009	193883010	FF	10/16/07	193883021	193883022
6	9/24/07	193883011	193883012				

(1) All samples were exchanged between 10:30AM and 11:00AM on the date shown.

Tables 4 and 5 summarize the analytical results and counting uncertainties determined in the SLF and final filters (FF) with the total activities summated. These results form the core elements to determine the solubility rates.

Table 4: Sample 1 Data Results Summary

Sample 1 (all activity reported in pCi/sample)						
Day	Pu-238 activity with 2 sigma uncertainty		Pu-239/240 activity with 2 sigma uncertainty		Am-241 activity with 2 sigma uncertainty	
1	3.18E+02	4.59E+01	2.70E+02	4.02E+01	1.45E+03	2.07E+02
2	1.41E+03	1.67E+02	1.20E+03	1.44E+02	4.58E+03	6.77E+02
3	1.08E+03	1.39E+02	8.06E+02	1.06E+02	2.24E+03	3.56E+02
4	7.18E+02	8.99E+01	5.45E+02	7.05E+01	1.02E+03	1.45E+02
5	3.32E+02	4.47E+01	2.96E+02	4.07E+01	6.44E+02	9.69E+01
6	1.18E+02	2.07E+01	1.19E+02	2.08E+01	1.94E+02	3.63E+01
7	2.19E+02	3.21E+01	1.72E+02	2.68E+01	3.56E+02	6.32E+01
14	5.88E+02	1.35E+02	4.01E+02	9.97E+01	9.92E+02	1.31E+02
21	3.25E+02	8.62E+01	2.74E+02	7.59E+01	3.87E+02	5.58E+01
28	2.24E+02	6.02E+01	1.56E+02	4.68E+01	4.20E+02	6.01E+01
FF	1.16E+03	1.23E+02	1.02E+03	1.10E+02	1.45E+03	1.77E+02
total	6.49E+03		5.26E+03		1.37E+04	

Table 5: Sample 2 Data Results Summary

Sample 2 (all activity reported in pCi/sample)						
Day	Pu-238 activity with 2 sigma uncertainty		Pu-239/240 activity with 2 sigma uncertainty		Am-241 activity with 2 sigma uncertainty	
1	7.78E+02	9.66E+01	6.61E+02	8.34E+01	2.93E+03	4.26E+02
2	6.97E+02	8.98E+01	5.68E+02	7.51E+01	1.88E+03	3.32E+02
3	3.87E+02	5.12E+01	3.10E+02	4.27E+01	7.72E+02	1.25E+02
4	3.21E+02	4.46E+01	2.78E+02	3.97E+01	5.67E+02	8.65E+01
5	2.21E+02	3.33E+01	1.95E+02	3.03E+01	3.77E+02	6.23E+01
6	2.86E+02	3.95E+01	2.46E+02	3.50E+01	4.78E+02	7.45E+01
7	1.45E+02	2.45E+01	1.08E+02	1.99E+01	2.06E+02	3.82E+01
14	4.03E+02	1.04E+02	3.38E+02	9.14E+01	5.43E+02	7.52E+01
21	2.12E+02	5.87E+01	1.78E+02	5.24E+01	3.33E+02	5.05E+01
28	1.62E+02	5.85E+01	2.01E+02	6.76E+01	2.17E+02	3.51E+01
FF	5.28E+02	6.46E+01	4.54E+02	5.69E+01	5.76+02	7.79E+01
total	4.14E+03		3.54E+03		8.88E+03	

A notable difference occurred on day one of the extraction as is shown graphically below in Figures 4 and 5. Sample one leached less activity on the first day as compared with the second day while sample two dropped in leached activity from day one to day two. This inversion in sample one is difficult to explain since nothing unusual was noticed during the experiment. It is possible that an air pocket formed in a portion of the material on the first addition of SLF and this could have caused the extraction to take place at a reduced rate. The issue was apparently overcome after the first day since the curves follow an exponential decay after day two. The anomaly may have manifest itself in the fitted exponential equations for Sample 1 since the two fractions do not add to one. For this reason the data was normalized to one in tables 8 and 9. Sample 2 required no normalization and in our opinion should be considered as the more reliable data set. All results are given throughout this report for evaluation and comparison.

The results summarized in Tables 4 and 5 with activities observed in the SLF were corrected to represent the insoluble portion remaining on the filter. The insoluble activity was calculated as the total initial activity on the filter (A_{total}) minus the cumulative activity collected in each of the 10 SLF extracts (A_i) as shown in Table 6. This determination was made using Equation 1 below.

Equation 1:
$$A_{INSOL} = A_{Total} - \sum_{i=1}^{10} A_i$$

The percent insoluble activity ($\%_{Insol}$) was determined from the insoluble activity divided by the total activity in the sample and is expressed as a percentage of the whole.

Equation 2:
$$\%_{INSOL} = 100 * \frac{A_{Total} - \sum_{i=1}^{10} A_i}{A_{Total}}$$

Figure 4: Sample 1 Graphical Depiction of Activity Leached Over Time

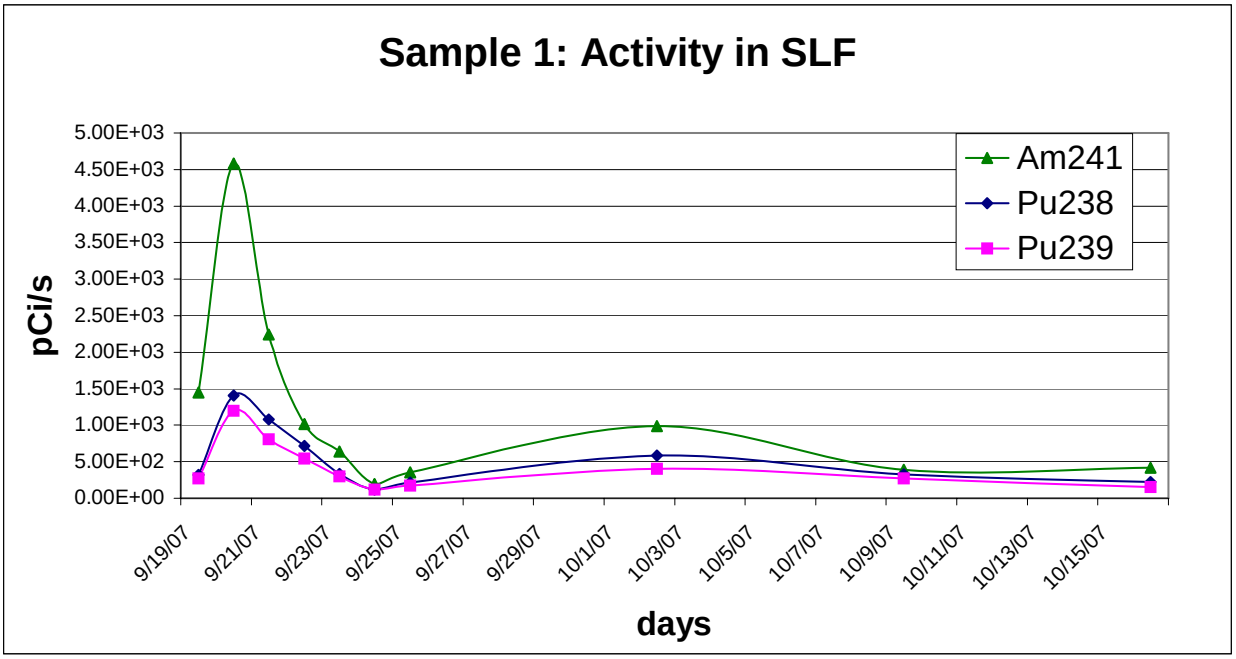


Figure 5: Sample 2 Graphical Depiction of Activity Leached Over Time

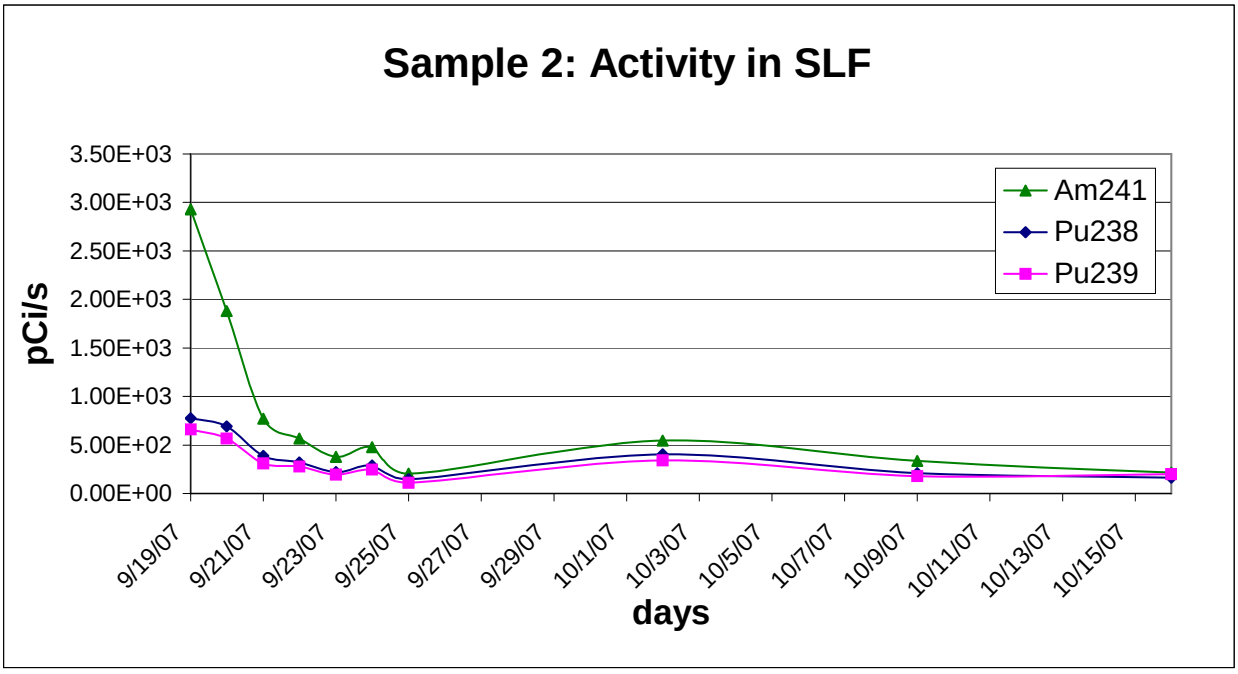
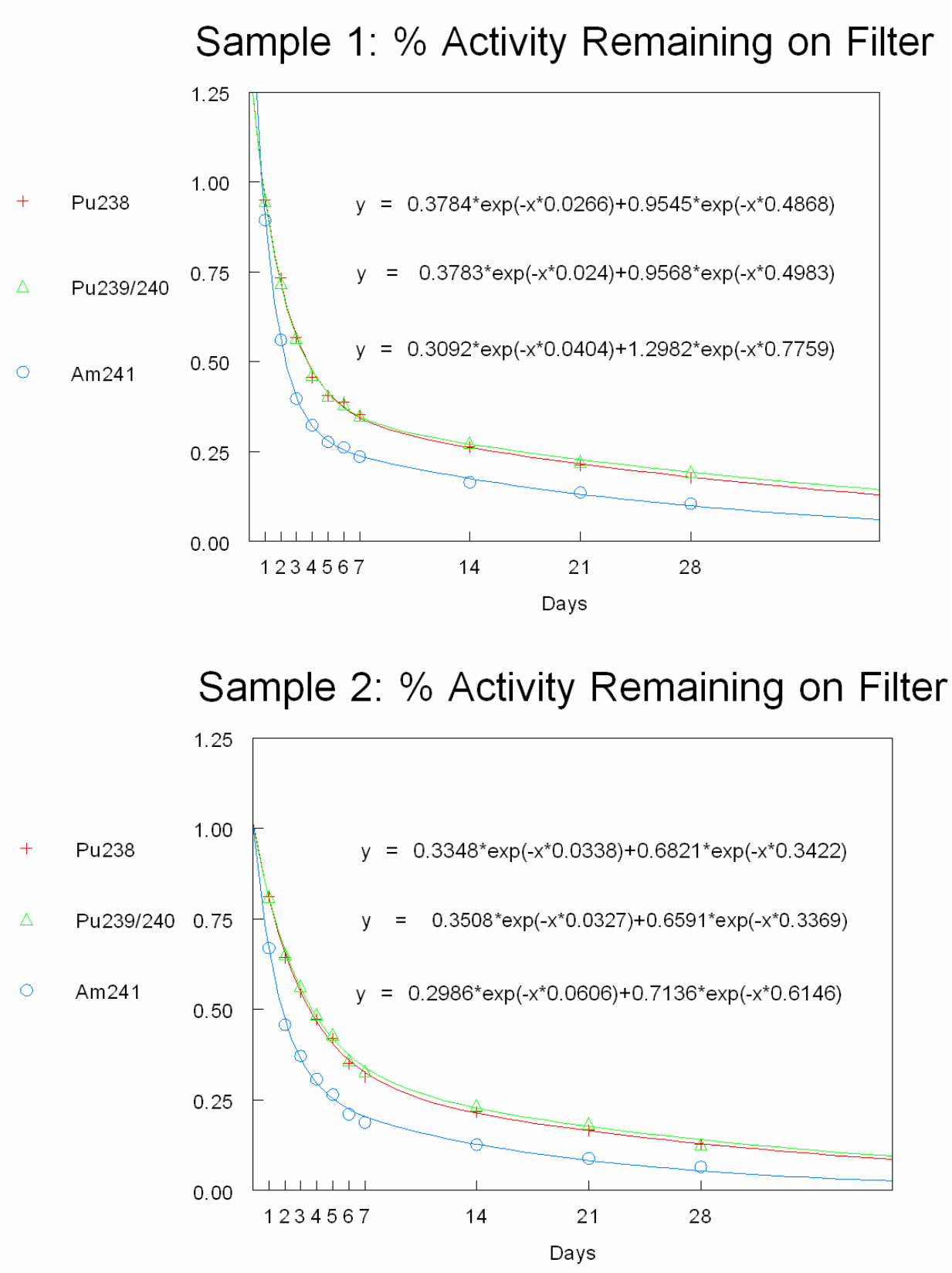


Table 6: Insoluble Activity and Percentages From Raw Data

Sample 1						
Day	Total Calculated Pu-238 Activity Remaining on Filter (pCi/sample)	Percent of Total Pu-238 Activity Remaining on Filter	Total Calculated Pu-239/240 Activity Remaining on Filter (pCi/sample)	Percent of Total Pu-239/240 Activity Remaining on Filter	Total Calculated Am-241 Activity Remaining on Filter (pCi/sample)	Percent of Total Am-241 Activity Remaining on Filter
1	6.17E+03	95.10%	4.99E+03	94.87%	1.23E+04	89.44%
2	4.76E+03	73.38%	3.79E+03	72.05%	7.70E+03	56.09%
3	3.68E+03	56.75%	2.98E+03	56.72%	5.46E+03	39.78%
4	2.97E+03	45.69%	2.44E+03	46.36%	4.44E+03	32.35%
5	2.63E+03	40.57%	2.14E+03	40.73%	3.80E+03	27.66%
6	2.52E+03	38.76%	2.02E+03	38.47%	3.61E+03	26.25%
7	2.30E+03	35.38%	1.85E+03	35.20%	3.25E+03	23.66%
14	1.71E+03	26.32%	1.45E+03	27.57%	2.26E+03	16.43%
21	1.38E+03	21.32%	1.18E+03	22.36%	1.87E+03	13.62%
28	1.16E+03	17.87%	1.02E+03	19.40%	1.45E+03	10.56%
Sample 2						
Day	Total Calculated Pu-238 Activity Remaining on Filter (pCi/sample)	Percent of Total Pu-238 Activity Remaining on Filter	Total Calculated Pu-239/240 Activity Remaining on Filter (pCi/sample)	Percent of Total Pu-239/240 Activity Remaining on Filter	Total Calculated Am-241 Activity Remaining on Filter (pCi/sample)	Percent of Total Am-241 Activity Remaining on Filter
1	3.36E+03	81.19%	2.88E+03	81.31%	5.95E+03	67.00%
2	2.67E+03	64.42%	2.31E+03	65.25%	4.07E+03	45.83%
3	2.28E+03	55.06%	2.00E+03	56.49%	3.30E+03	37.13%
4	1.96E+03	47.30%	1.72E+03	48.63%	2.73E+03	30.75%
5	1.74E+03	41.96%	1.53E+03	43.12%	2.35E+03	26.50%
6	1.45E+03	35.05%	1.28E+03	36.16%	1.88E+03	21.12%
7	1.31E+03	31.54%	1.17E+03	33.11%	1.67E+03	18.80%
14	9.02E+02	21.80%	8.33E+02	23.55%	1.13E+03	12.68%
21	6.90E+02	16.68%	6.55E+02	18.52%	7.93E+02	8.93%
28	5.28E+02	12.76%	4.54E+02	12.84%	5.76E+02	6.49%

Figure 6: Exponential Curves from SlideWrite Plus™



The data in Table 6 and Figure 6 were fit to a two-term exponential function of the form:

Equation 3:
$$F_t = f_1 e^{k_1 t} + f_2 e^{k_2 t}$$

Where f_i represents the fraction of component i being solubilized with the removal rate constant k_i. The results of these fits are provided in Table 7. Note that the rapid fraction in the equation equates to the portion with the higher K term. Table 8 shows the rapid and slow fractions along with their associated half times as determined from Equation 4.

Equation 4:
$$T_{1/2} = \frac{0.693}{k_i}$$

Where 0.693 is the natural log of 2 and *Ki* is the exponent derived from the curve fit.

Table 7: Results of Curve Fits for Fraction Remaining on Filter

		Slower Clearing Component		Faster Clearing Component		
Sample Number	Isotope	f_1	k_1	f_2	k_2	Fit Correlation Coefficient, r^2
1	Pu-238	0.3784	0.0266	0.9545	0.4868	0.9986
	Pu-239/240	0.3783	0.0240	0.9568	0.4983	0.9995
	Am-241	0.3092	0.0404	1.2982	0.7759	0.9999
2	Pu-238	0.3348	0.0338	0.6821	0.3422	0.9986
	Pu-239/240	0.3508	0.0327	0.6591	0.3369	0.9983
	Am-241	0.2986	0.0606	0.7136	0.6146	0.9976

Table 8 provides a summary of the fit coefficients in terms of rapid and slow dissolved fractions and clearance half times.

Table 8: Fractions and Half Time Summary

	Isotope	Fraction Dissolved Rapidly	Half Time (days)	Fraction Dissolved Slowly	Half Time (days)
Sample 1	Pu238	71.6%	1.42	28.4%	26.04
	Pu239/240	71.7%	1.39	28.3%	28.92
	Am241	80.8%	0.89	19.2%	17.14
Sample 2	Pu238	68.2%	2.03	33.5%	20.49
	Pu239/240	65.9%	2.06	35.1%	21.22
	Am241	71.4%	1.13	29.9%	11.43

Note: Sample 1 was normalized to 1 in order to estimate the rapid and slow fractions

Table 9 provides a comparison of the observed deposition fractions along with the associated clearance rate function as provided in Table 7 along with the assumed values for the ICRP 66 lung model for each of the three solubility classes.

Table 9: Comparison of Solubility Data with ICRP 66

		Type F (fast)	Type M (moderate)	Type S (slow)	Sample 1	Sample 2	ICRP Solubility Class
Pu238	Fraction dissolved rapidly (F_r)	1.0	0.1	0.001	0.716	0.682	M
	Rapid dissolution rate, s_r (d^{-1})	100	100	100	0.487	0.342	M
	Slow dissolution rate, s_s (d^{-1})	0	0.005	0.0001	0.027	0.034	M
Pu239240	Fraction dissolved rapidly (F_r)	1.0	0.1	0.001	0.717	0.659	M
	Rapid dissolution rate, s_r (d^{-1})	100	100	100	0.498	0.337	M
	Slow dissolution rate, s_s (d^{-1})	0	0.005	0.0001	0.024	0.033	M
Am241	Fraction dissolved rapidly (F_r)	1.0	0.1	0.001	0.808	0.714	M
	Rapid dissolution rate, s_r (d^{-1})	100	100	100	0.776	0.615	M
	Slow dissolution rate, s_s (d^{-1})	0	0.005	0.0001	0.040	0.061	M

Note: Sample 1 was normalized to 1 in order to estimate the rapid and slow fractions

Summary

Overall the data suggests the study material had solubility in the SLF between type F (fast) and M (moderate) characteristics. Two decay rates were observed in the study and are shown mathematically by the curve fits. Since type F material is expected to follow a single exponential decay, the dual exponential curves suggest type M material. Tables 8 and 9 show the larger fraction of the two components contributed from 65% to 81% of the whole and dissolved with a shorter half time than the smaller fractions. Type M material would be expected to have a rapidly dissolving component of at least 10%. The curve fits used to correlate the solubility rates were derived from the percentages of material remaining undissolved on the filters over time (Cheng ET. AL. 2004). The percentage of undissolved material was fitted to the exponential equations shown using the graphing program SlideWrite Plus™. The data shows good correlation between americium and plutonium isotopes with americium being slightly more soluble in lung fluid than the plutonium isotopes.

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