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DISSOLUTION RATES OF URANIUM COMPOUNDS IN SIMULATED LUNG FLUID

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ABSTRACT

Maximum dissolution rates of uranium into simulated lung fluid from a variety of materials were measured at 37°C in order to estimate clearance rates from the deep lung. A batch procedure was utilized in which samples containing as little as 10 µg of natural uranium could be tested. The materials included: products of uranium mining, milling and refining operations, coal fly ash, an environmental sample from a site exposed to multiple uranium sources, and purified samples of $(\text{NH}_4)_2\text{U}_2\text{O}_7$, U_3O_8 , UO_2 , and UF_4 . Dissolution of uranium from several materials indicated the presence of more than one type of uranium compound; but in all cases, the fraction F of uranium remaining undissolved at any time t could be represented by the sum of up to three terms in the series: $F = \sum_i f_i \exp(-0.693t/T_i)$, where f_i is the initial fraction of component i with dissolution half-time T_i . Values of T_i varied from 0.01 day to several thousand days depending on the physical and chemical form of the uranium. Dissolution occurred predominantly by formation of the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ion; and as a result, tetravalent uranium compounds dissolved slowly. Dissolution rates of size-separated yellow-cake aerosols were found to be more closely correlated with specific surface area than with aerodynamic diameter.

INTRODUCTION

The radioactivity and chemical toxicity of uranium compounds cause concern about health risks which may arise from breathing aerosols of uranium-

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bearing materials. Such aerosols are encountered in a wide variety of forms, not only in the uranium mining and processing industries but also at plants where phosphate fertilizers are produced (ref. 1) and coal is burned (ref. 2). It is generally agreed that proper assessment of these risks requires knowledge of the clearance rates for these materials from the deep lung. The International Commission on Radiological Protection has recognized this fact by incorporating such parameters in a model for describing the residence times of foreign substances in the lung and other organs of the human body (ref. 3). In the absence of direct measurements, lung-clearance rates are usually approximated by dissolution rates in vitro. This action is supported by experiments which indicated that after the first few days following aerosol deposition, dissolution was the principal mode of clearance from the lower respiratory tract of dogs (refs. 4,5). This paper summarizes the methods and results of several related studies at this laboratory with the objective of measuring the dissolution rates of various uranium-bearing materials in simulated lung fluid at 37°C.

Experiments are also described herein which reveal aspects of the uranium dissolution mechanism as well as limitations in predicting the biological availability of uranium from aerosols. One of the major factors which impedes accurate prediction of lung-clearance rates and dissolution rates of inhaled aerosols is the variety in stoichiometric and crystalline forms of uranium compounds. For example, there are at least four uranium oxides; and in each case, the oxygen:uranium ratio can vary rather widely and continuously about a central value (ref. 6). In addition, there are at least seven crystalline forms of the compounds represented by the formula UO_3 , and several of these can exist in one or more hydrated forms (ref. 6). Thus, there are ample possibilities for change in the stoichiometry or crystalline form of uranium on aerosols due to interactions with their environment.

MATERIALS AND METHODS

Sources and Characterization of Samples

A variety of uranium-bearing materials were used in the dissolution trials. Samples of uranium ore and yellow cake were obtained from the

Kerr-McGee Nuclear Corporation, Oklahoma City, OK. Only particles with diameters less than 45 μm were used for the dissolution trials, and their specific surface areas were measured with a Micromeritics Surface Area Analyzer. One of the yellow-cake samples was fractionated with a Bahco Micro-particle Classifier into particles with measured aerodynamic diameters. Baghouse ash from a coal-fired power plant was obtained from the GCA Corporation, Bedford, MA. This sample was also fractionated into particles with measured aerodynamic diameters. An airborne environmental sample was collected in southern Illinois at a site exposed to both coal fly ash from a large power plant and stack exhaust from a plant converting yellow cake to UF_6 . The particles used for the dissolution trial had aerodynamic diameters in the 0 to 5.5- μm range as determined by their escaping a cyclone pre-separator adjusted to retain larger particles. Aerosol samples were also obtained from various locations in a plant where light-water-reactor fuel rods are fabricated, courtesy of the General Electric Company, Wilmington, NC. All particles in these samples were less than 50 μm in diameter. Purified ammonium diuranate was obtained as a gift from the Westinghouse Electric Corporation, Columbia, SC; and uranium octoxide was obtained from the U. S. Bureau of Standards as Standard Reference Material 950. Portions of these substances which contained particles less than 125 μm in diameter were used for the dissolution trials; and their specific surface areas were also measured. Samples of purified uranium dioxide and tetrafluoride were obtained from the New Brunswick Laboratory of the U. S. Department of Energy, Argonne, IL; and portions containing particles less than 45 μm in diameter were used for the dissolution trials.

Preparation of Simulated Lung Fluid

The electrolyte compositions of human interstitial lung fluid and the simulant used in these studies are shown in Table 1. Comparison shows that they are almost identical. The protein components of actual lung fluid were represented by an ionically equivalent amount of citrate in the simulant as suggested by Moss (ref. 8). Lung-fluid proteins are poorly characterized and generally not available in large quantities, and substitute proteins hinder filtration and promote bacterial growth in solutions. Phospholipids,

also known to be present in trace amounts in actual lung fluid, were not included in the simulant for the same reasons.

TABLE 1

Compositions of actual and simulated lung fluids

Ion	Actual (ref. 7)	Simulated (ref. 8)
Calcium, Ca^{2+}	5.0 meq/l	5.0 meq/l
Magnesium, Mg^{2+}	2.0 "	2.0 "
Potassium, K^{+}	4.0 "	4.0 "
Sodium, Na^{+}	<u>145.0</u> "	<u>145.0</u> "
Total Cations	156.0 "	156.0 "
Bicarbonate, HCO_3^{-}	31.0 meq/l	31.0 meq/l
Chloride, Cl^{-}	114.0 "	114.0 "
Citrate, $\text{H}_5\text{C}_6\text{O}_7^{3-}$	--	1.0 "
Acetate, $\text{H}_3\text{C}_2\text{O}_2^{-}$	7.0 "	7.0 "
Phosphate, HPO_4^{2-}	2.0 "	2.0 "
Sulfate, SO_4^{2-}	1.0 "	1.0 "
Protein	<u>1.0</u> "	<u>---</u>
Total Anions	156.0 "	156.0 "
pH	7.3-7.4	7.3-7.4

Simulated lung fluid with the composition shown in Table 1 was prepared by slowly adding the following ingredients in order to 990 ml of distilled water and adjusting the final volume to 1000 ml:

0.2033 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
 6.0193 g NaCl
 0.2982 g KCl
 0.2680 g $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$
 0.0710 g Na_2SO_4
 0.3676 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
 0.9526 g $\text{NaH}_3\text{C}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$
 2.6043 g NaHCO_3
 0.0970 g $\text{Na}_3\text{H}_3\text{C}_6\text{O}_7 \cdot 2\text{H}_2\text{O}$

If the pH of the resulting solution was not 7.3-7.4, it was adjusted to this value with small volumes of 1 N HCl.

Dissolution Technique

Techniques were aimed at measuring the maximum dissolution rates of each sample in SLF at 37°C since the lung is expected to be a site for efficient dissolution. Although several techniques were tested, maximum dissolution rates were achieved most easily in simple suspensions of the samples in SLF. Diffusion-limited rates were avoided by agitating the suspended samples vigorously, filtering the suspensions frequently and replacing the aqueous phase with fresh SLF. Typically, suspensions were filtered after 0.1, 0.2, 0.3, 1, 3, 10, 20, 30, and 60 days. Each filtrate was then analyzed for uranium to determine how much had dissolved during the various periods of the trial.

Fig. 1 illustrates the dissolution chamber that was used for many of the trials. It consisted of a 5-ml, conical bottom vial with Teflon-lined screw cap containing 5.00 ml of SLF and a Teflon-coated magnetic stirrer. The system was stirred and maintained at $37 \pm 1^\circ\text{C}$ by placing the vial in a heating block/stirrer assembly (Pierce Chemical Co.). After thermal equilibrium was attained, up to 0.2 gram of sample was added to the vial. After selected time periods, the vial was removed from the heating block and centrifuged to force the undissolved dust into the conical end. The cap was then opened, and the supernatant fluid was drawn through a stainless steel needle into a plastic syringe. A membrane filter (Millipore, 13-mm diameter, GC, 0.2 μm pore size) in a stainless steel filter holder (Millipore, Swinnex) was fitted on the end of the syringe, and the solution was filtered into a container and stored for uranium analysis. The membrane filter was then removed with stainless steel forceps, and 5.00 ml of fresh SLF was added to the barrel of the syringe. The filter holder, minus filter, and the syringe needle were refitted on the syringe; and the small amount of solid sample held on the filter was washed off into the vial with a jet of SLF from the syringe. The vial was then capped, vortexed to resuspend all the remaining sample and replaced in the heating block. The pH of the suspension was checked every three days and adjusted to 7.3-7.4 with dilute HCl, if necessary. At the end of 60 days, the residual sample was dissolved in 5.00 ml of warm concentrated nitric acid and analyzed for uranium.

Fig. 1. Cross-section of sample container for dissolution by the mini-batch technique.

When larger amounts of sample were available, the "mini-batch" technique described above was occasionally scaled up, keeping the volume ratio of SLF to sample above 10. Thus, dissolutions of uranium-ore and yellow-cake were conducted in 100-ml portions of SLF contained in 125-ml, glass-stoppered Erlenmeyer flasks and placed on a shaker bath at 37°C. Dissolution of fly ash was conducted in 900 ml of SLF contained in 1000-ml round-bottom flasks and stirred with Teflon paddles.

Analysis of Uranium

Three methods were used for the analysis of uranium in the filtrates and acid-dissolved residues. ASTM procedure D2907-75 (ref. 9) was used most frequently, and it allowed testing of samples initially containing as little as 10 µg of uranium. It involved extraction of uranium from the aqueous solutions with tetrapropylammonium hydroxide and hexone, followed by fluorometric analysis of the extract. Alternatively, the method of Maeck, et al. (ref. 10) was used. This involved colorimetric determination of uranium with dibenzoylmethane following a similar extraction with tetrapropylammonium hydroxide and hexone. A third method, direct photometry in 1-dm spectrophotometer cells at 448 nm, was used on filtrates from the dissolution trials of yellow-cake samples. The concentration of uranium in a filtrate was obtained by dividing the measured absorbance by 1.005 lg⁻¹dm⁻¹, the absorptivity of uranium in this medium.

Evaluation of Dissolution Rates

Dissolution rates were expressed as times for half dissolution since theory indicates that the fraction of a pure sample remaining undissolved should decrease exponentially with time, unless the particle-size range is very broad (ref. 11). Since the purities of the samples were uncertain, the data were allowed to fit an equation of the form:

$$F = \sum_i f_i \exp (-0.693t/T_i)$$

where F is the fraction of total uranium remaining undissolved after time t, and the f_i are the initial weight fractions of uranium components in the sample with dissolution half-times T_i. The values of F were calculated by

subtracting the amount of uranium dissolved during any sampling period from the amount undissolved at the beginning of that period and dividing this quantity by the total amount of uranium in the sample. Preliminary values of f_i and T_i were obtained by graphical analysis of the data; and these were then used as starting values in an iterative computer program to obtain the best fit to data by regression analysis.

RESULTS

Yellow cake and $(\text{NH}_4)_2\text{U}_2\text{O}_7$

"Yellow cake" is the target product of most uranium milling processes. The composition of freshly prepared yellow cake is that of ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$, but exposure to hot-air dryers and aging can significantly change its color and composition. Fig. 2 shows the dissolution behavior of purified ammonium diuranate and a fresh, mill-generated aerosol of yellow cake. The pure compound dissolved completely with a single dissolution half-time of 0.2 days; and while most of the yellow-cake sample displayed this behavior, a second, more slowly dissolving component was evident. After a year of aging, yellow cake from the same plant still showed two components with different dissolution rates, but their proportions had equalized. Also, the fraction of more-rapidly dissolving component was more closely correlated with specific surface area than with aerodynamic diameter, as shown in Table 2.

TABLE 2

Dissolution parameters of uranium from yellow-cake samples as a function of aerodynamic diameter and specific surface area

<u>Diameter</u>	<u>Area</u>	<u>f_1</u>	<u>T_1</u>	<u>f_2</u>	<u>T_2</u>
1 to 3 μm	4.7 m^2g^{-1}	0.65	1.3 d	0.35	51 d
7 to 13	4.3	0.60	1.3	0.40	62
18 to 44	3.4	0.40	0.9	0.60	89

Fig. 2. Dissolution of ammonium uranate and yellow cake in simulated lung fluid at 37°C

Ammonium diuranate and yellow-cake samples did not dissolve at detectable rates, i.e., T was greater than 10,000 days if bicarbonate ion was omitted from the SLF. The optical absorption spectrum of ammonium diuranate in complete SLF is shown in Fig. 3. This spectrum exactly matches that published for the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ anion (ref. 12). Similar spectra, differing only in absorption intensity, were obtained for all samples that underwent appreciable dissolution.

Uranium ore, U_3O_8 , UO_2 and UF_4

Uranium in samples of ore aerosols was found to dissolve in SLF with a single dissolution half-time of around 60 days, as shown in Table 3.

TABLE 3

Dissolution parameters of uranium from uranium-ore samples as a function of specific surface area

<u>Sample No.</u>	<u>Area</u>	<u>f_1</u>	<u>T_1 (90% Confidence Interval)</u>
1	6.0 m^2g^{-1}	1.00	50-167 d
2	5.2	1.00	57-82
3	3.6	1.00	46-63

In contrast, uranium octoxide and uranium dioxide, two of the most stable oxides of uranium, and uranium tetrafluoride did not dissolve at detectable rates.

Coal fly ash

Dissolution of uranium from coal fly ash indicated the presence of two uranium components, as shown in Table 4. There was some indication that the fraction of more rapidly dissolving component increased as the particle size decreased, but the effect was not large.

TABLE 4

Dissolution parameters of uranium from coal fly-ash samples as a function of aerodynamic diameter and uranium concentration

<u>Diameter</u>	<u>Uranium Concentration</u>	<u>f_1</u>	<u>T_1</u>	<u>f_2</u>	<u>T_2</u>
<0.5 μm	47 $\pm$ 5 $\mu\text{g/g}$	0.08	2.9 d	0.92	2900 d.
0.5 to 1.0	35 $\pm$ 4	.03	2.9	.97	3100
1.0 to 3.0	22 $\pm$ 2	.05	3.2	.95	3300
3.0 to 10	14 $\pm$ 1	.04	3.8	.96	2600
10 to 15	10 $\pm$ 1	.04	3.6	.96	2800

Fig. 3. Optical absorption spectrum of ammonium diuranate dissolved in simulated lung fluid

LWR-fuel plant materials

The dissolution half-times of uranium from aerosols collected in a plant manufacturing light-water-reactor (LWR) fuel elements are shown in Table 5. As expected, they are strongly influenced by the type of compound in the process line at each sampling site; but they also indicated the degree of mixing between different aerosol sources.

TABLE 5

Dissolution parameters of uranium from aerosol samples collected at various sites in a LWR-fuel element manufacturing plant

Site	Site Product	f_1	T_1	f_2	T_2
Vaporizer/dissolver	UF_6 , UO_2F_2	0.90	0.01 d	0.10	172 d
Calciner entrance	$(NH_4)_2U_2O_7$	0.63	5.3	0.37	$>10^4$
Calciner discharge	U_3O_8	0.01	0.01	0.99	$>10^4$
Pellet press	UO_2 (unsintered)	0.04	0.01	0.96	$>10^4$
Pellet grinder	UO_2 (sintered)	0.03	0.01	0.97	$>10^4$

Environmental material

Table 6 shows the dissolution half-times of uranium from the aerosol collected at the site exposed to multiple sources of uranium-bearing materials. The dissolution data indicate that at least three uranium components were present.

TABLE 6

Dissolution parameters of uranium from an aerosol sample collected at a site exposed to both coal fly ash and uranium-processing effluents

f_1	T_1	f_2	T_2	f_3	T_3
0.24	0.09 d	0.11	0.69 d	0.65	1900 d

DISCUSSION AND CONCLUSIONS

The preceding results show that the dissolution half-times of uranium from various uranium-bearing materials into simulated lung fluid at 37°C cover a wide range of values, from 0.01 days to greater than 10,000. The insolubility of ammonium diuranate in SLF devoid of bicarbonate ion and the

detection of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ in filtrates from many of the dissolution trials indicate that the rate-determining step in the dissolution process can be represented by the equation:

where $(\text{NH}_4)_2\text{U}_2\text{O}_7$ can be replaced by any compound of hexavalent uranium. Although acetate and citrate ions are known to form soluble anionic complexes with hexavalent uranium, their complexing abilities or concentrations in SLF appear to be too low to affect the dissolution rates. Tetravalent uranium compounds do not form strong complexes with carbonate ion; and hence, their dissolution must depend on reactions such as

In the studies described here, the suspensions were exposed to air-saturated solutions of SLF throughout the dissolution trial, but the resulting oxygen tension may have been too low to allow the reaction cited above to occur at a significant rate. Such conditions, of course, would also prevail in the lung.

The technique described above provides precise dissolution data inexpensively. Although a complete numerical analysis of the dissolution process generally requires data from a 60-day dissolution trial, shorter trials may be adequate in some cases. This analysis automatically allows for multiple forms of uranium in the samples and does not depend upon identification of these forms. As the examples show, it can easily provide data which portrays variations in the biological availability of uranium with respect to either time or location. Additional experiments are needed to correlate dissolution half-times in SLF with lung-clearance rates in vivo, and it is hoped that the technique and results presented here will facilitate such comparisons.

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