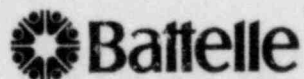

**Solubility Classification of
Airborne Uranium Products
Collected at the Perimeter of
the Allied Chemical Plant,
Metropolis, Illinois**

D. R. Kalkwarf

May 1980

Prepared for the
U.S. Nuclear Regulatory Commission

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute



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SOLUBILITY CLASSIFICATION OF
AIRBORNE URANIUM PRODUCTS
COLLECTED AT THE PERIMETER OF
THE ALLIED CHEMICAL PLANT,
METROPOLIS, ILLINOIS

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Richland, Washington 99352

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METROPOLIS, ILLINOIS

SUMMARY

Airborne uranium products were collected at the perimeter of the uranium-conversion plant operated by the Allied Chemical Corporation at Metropolis, Illinois, and the dissolution rates of these products were classified in terms of the ICRP Task Group Lung Model. Assignments were based on measurements of the dissolution half-times exhibited by uranium components of the dust samples as they dissolved in simulated lung fluid at 37°C. Based on three trials, the dissolution behavior of dust with aerodynamic equivalent diameter (AED) less than 5.5 μm and collected nearest the closest residence to the plant was classified 0.40 D, 0.60 Y. Based on two trials, the dissolution behavior of dust with AED greater than 5.5 μm and collected at this location was classified 0.37 D, 0.63 Y. Based on one trial, the dissolution behavior of dust with AED less than 5.5 μm and collected at a location on the opposite side of the plant was classified 0.68 D, 0.32 Y. There was some evidence for adsorption of dissolved uranium onto other dust components during dissolution, and preliminary dissolution trials are recommended for future samples in order to optimize the fluid replacement schedule.

TABLE OF CONTENTS

SUMMARYiii
TABLE OF CONTENTS	v
FIGURESvii
TABLES	ix
INTRODUCTION	1
CONCLUSIONS AND RECOMMENDATIONS	2
PROCEDURE	3
SAMPLE COLLECTION	3
SAMPLE PREPARATION	3
PREPARATION OF SIMULATED LUNG FLUID	5
DISSOLUTION TECHNIQUE	6
URANIUM ANALYSES	7
EVALUATION OF DISSOLUTION HALF-TIMES	9
RESULTS	9
SAMPLE COLLECTION AND ANALYTICAL DATA	9
DISSOLUTION BEHAVIOR OF THE SAMPLES	10
SOLUBILITY CLASSIFICATIONS	23
DISCUSSION	23
REFERENCES	25
ACKNOWLEDGMENTS	26

FIGURES

1. Location of Sampling Stations with Respect to the Plant	4
2. Cross Section of Dissolution Chamber for Dust Samples	8
3. Dissolution of Portions RD11-1 (◦), RD11-2 (Δ) AND RD11-3 (◻)	13
4. Dissolution of Portions ND11-1 (∇) and ND11-2 (Δ).	14
5. Dissolution of Portion RD02-1	15

TABLES

1. Compositions of Actual and Simulated Lung Fluids	5
2. Collection Data for Sample RD11.	10
3. XRF Analyses of the Solid Samples.	11
4. Specifications of Sample Portions.	12
5. Incremental Amounts of Uranium Dissolved and Fraction. of Total Uranium Remaining Undissolved During Dissolution of Sample RD11-1	16
6. Incremental Amounts of Uranium Dissolved and Fraction. of Total Uranium Remaining Undissolved During Dissolution of Sample RD11-2	17
7. Incremental Amounts of Uranium Dissolved and Fraction. of Total Uranium Remaining Undissolved During Dissolution of Sample RD11-3	18
8. Incremental Amounts of Uranium Dissolved and Fraction. of Total Uranium Remaining Undissolved During Dissolution of Sample ND11-1	19
9. Incremental Amounts of Uranium Dissolved and Fraction. of Total Uranium Remaining Undissolved During Dissolution of Sample ND11-2	20
10. Incremental Amounts of Uranium Dissolved and Fraction. of Total Uranium Remaining Undissolved During Dissolution of Sample RD02-1	21
11. Dissolution Parameters of Uranium Compounds in the Sample Portions	22
12. 95% Confidence Intervals for the Dissolution Parameters.	22
13. Uranium Solubility Classifications for Dust Collected. Near the Allied Plant	23

INTRODUCTION

The purpose of this study was to collect airborne uranium products at the perimeter of the uranium-conversion plant operated by the Allied Chemical Corporation at Metropolis, Illinois, and to classify the dissolution rates of these products in terms of the ICRP Task Group Lung Model.¹ The International Commission on Radiological Protection developed this model for use in computing the radiation dose from radionuclides deposited in the lung. A key parameter is the classification of the deposited material according to the rate at which it leaves the lung. Three classes were established: D, W, and Y, corresponding to half-times in the lung of 0 to 10 days, 11 to 100 days, and >100 days, respectively. If clearance of the material from the lung is not strictly exponential with time, it is approximated by a sum of exponentials; and the material is classified according to the fractions of D, W, and Y components. In the absence of biological data, lung-clearance half-times for materials have been approximated by their dissolution half-times in simulated lung fluids.¹⁻³ Although endocytosis and ciliary-mucus transport are known to contribute to lung clearance, experiments have indicated that a few days after dust deposition, dissolution determines the clearance rate for the lower respiratory tract.^{4 5} Given the lung-clearance classification for a material, its transport rates between other anatomical compartments are automatically assigned. From these parameters, one can compute the residence times of the material and the associated radiation dose in each compartment.⁶

In the present study, the dust of main concern was that expected to reach the nearest resident to the plant. This was collected at a position on the plant perimeter as close to the nearest residence as could be achieved with the electric power system available. Dichotomous samples were used to separate dust with aerodynamic equivalent diameter (AED) less than 5.5 μm from dust with AED >5.5 μm . Initially, it was felt that this fractionation would separate respirable dust from non-respirable dust; but recently the U. S. Environmental Protection Agency has recommended that all particulates with <15 μm AED be considered inhalable for hazard evaluations.⁷ Both fractions, as well as dust with AED >5.5 μm from the opposite side of the plant,

were used for separate dissolution-rate determinations in vitro under conditions simulating those in the lung. Dissolutions were carried out at 37°C in an aqueous solution whose composition closely matched that for interstitial lung fluid. Maximum dissolution rates were sought by means of rapid agitation because the lung is expected to be a site for efficient dissolution and because the values were to approximate clearance rates that include contributions from endocytosis and ciliary-mucus transport.

CONCLUSIONS AND RECOMMENDATIONS

Dissolution rates of uranium from the samples into simulated lung fluid at 37°C could best be described by three-term equations of the form:

$$F = f_1 \exp(-0.693t/T_1) + f_2 \exp(-0.693t/T_2) + f_3 \exp(-0.693t/T_3)$$

where F is the fraction of total uranium remaining undissolved at any time and the T_i are the dissolution half-times of uranium components with initial weight fractions f_i in the sample. Two of the components in each sample had dissolution half-times between 0 and 10 days, and the third component had a dissolution half-time greater than 100 days. Based on three trials, the solubility classification of dust with AED $<5.5 \mu\text{m}$ and collected nearest the closest residence to the plant was found to be 0.40D, 0.60Y. Based on two trials, the solubility classification of dust with AED $>5.5 \mu\text{m}$ and collected at the same location was found to be 0.37D, 0.63Y. Based on one trial, the solubility classification of dust with AED $<5.5 \mu\text{m}$ and collected at the opposite side of the plant was found to be 0.68D, 0.32Y.

The dissolution technique developed in this study proved to be well suited for samples initially containing 10 to 100 μg of uranium. The optimum sample size and optimum replacement schedule for the simulated lung fluid (SLF) should be estimated after a scouting, dissolution trial with a portion of the sample. Reduction of sample size and increased frequency of SLF replacement should suppress adsorption of dissolved uranium onto soil or soot in the sample which would decrease the apparent dissolution rate of the uranium. However, this action must be tempered by consideration of the sensitivity and precision of the uranium assay method available. In addition, sterilization of the sample with ethylene oxide gas is recommended in order to insure against possible effects of bacterial growth in the dissolving suspension.

PROCEDURE

SAMPLE COLLECTION

Airborne dust was collected at three sites around the perimeter of the Metropolis works. These are shown on the map in Figure 1, and Station 11 is the site closest to the nearest residence. Samples were collected with high-volume air samplers (General Metal Works, Model GMWL 2000) operating at 40 cfm. The samplers were equipped with cyclone preseparators (Sierra Instruments, Model 230CP) which, according to the manufacturer's literature, collect dust particles with aerodynamic equivalent diameters (AED) greater than 5.5 μm when operated at 40 cfm. Particles with AED less than 5.5 μm were collected on 8" x 10" sheets of filter paper (Whatman 41). Four identical air samplers were used, and their sampling rates were adjusted daily to 40 cfm. The flow meters on the samplers were calibrated in our laboratory with a positive-displacement flow meter (Dresser Instruments, Model 5M125 Roots Meter). Each unit was protected by a steel housing, and the air intakes were positioned 4 ft off the ground. All four samplers were used at Station 11 from September 6 to 13 and from September 17 to October 3, 1979. The filters were changed every three days and stored in polyethylene bags, whereas the dust in the cyclone preseparators was removed weekly with a camel's hair brush and stored in a glass vial. During the period from September 14 to September 16, two samplers were used at Station 10 and two were used at Station 11. Two filters were used in each sampler during that time.

SAMPLE PREPARATION

Dust samples were dried, weighed and then divided with Allied Chemical personnel so that they could also conduct dissolution studies on these materials. The dust-coated cellulose filters were placed in a desiccator over anhydrous calcium sulfate (J. T. Baker, Drierite) for two or three days; and at the end of that time, the dust was "vacuumed off" the surface with a vacuum line fitted with a 25-mm diameter membrane filter (Millipore, Type HA in a Swinnex holder). The dust collected on the membrane filter was easily transferred into a glass vial with a camel's hair brush. Samples from the cyclone preseparators were also dried in the desiccator. Each of the samples was then thoroughly mixed with a mechanical shaker. The respirable dust

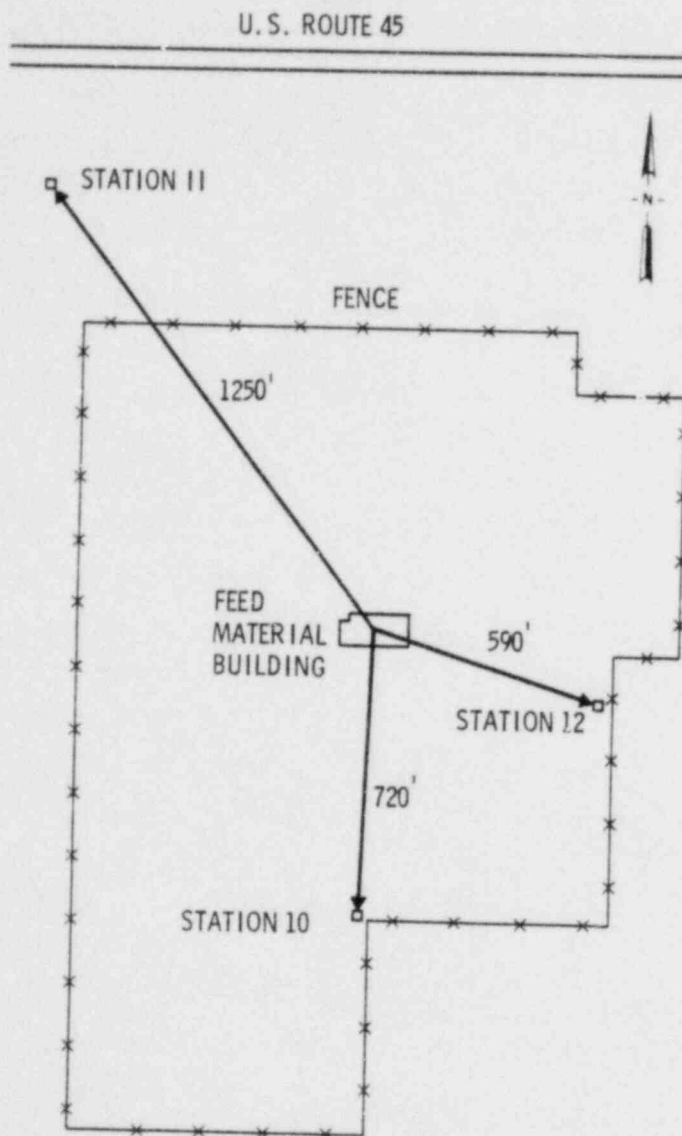


FIGURE 1. Location of Sampling Stations with Respect to the Plant

sample from Station 11 was designated RD11, the non-respirable dust sample from that station was designated ND11, and the respirable dust from Stations 10 and 12 was combined and designated sample RD02.

PREPARATION OF SIMULATED LUNG FLUID

The electrolyte compositions of human interstitial lung fluid and the simulant used in this study 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.⁹ 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. In a recent test,¹⁰ one of the suspected phospholipids, dipalmitoyl lecithin, was added to the simulant used in this experiment to form a 200 mg/l solution. No effect of this ingredient on the dissolution rate of uranium yellow cake samples was observed.

TABLE 1. Compositions of Actual and Simulated Lung Fluids

<u>Ion</u>	<u>Actual⁸</u>	<u>Simulated⁹</u>
Calcium, Ca ²⁺	5.0 meg/l	5.0 meg/l
Magnesium, Mg ²⁺	2.0 "	2.0 "
Potassium, K ⁺	4.0 "	4.0 "
Sodium, Na ⁺	145.0 "	145.0 "
Total Cations	156.0 "	156.0 "
Bicarbonate, HCO ₃ ⁻	31.0 "	31.0 "
Chloride, Cl ⁻	114.0 "	114.0 "
Citrate, H ₅ C ₆ O ₇ ³⁻	--	1.0 "
Acetate, H ₃ C ₂ O ₂ ⁻	7.0 "	7.0 "
Phosphate, HPO ₄ ²⁻	2.0 "	2.0 "
Sulfate, SO ₄ ²⁻	1.0 "	1.0 "
Protein	1.0 "	--
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 dis-

tilled 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 $\text{NaH}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$
2.6043 g NaHCO₃
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

Dissolution of each dust sample was conducted in stirred, 5.00-ml volumes of simulated lung fluid (SLF) at 37°C. The suspensions were contained in 5-ml reaction vials (Pierce Chemical, Reacti-Vial) with Teflon-coated magnetic stirrers and Teflon-lined screw caps, as shown in Figure 2. The vials were kept at the desired temperature in a heating block/stirrer assembly (Pierce Chemical, Reacti-Therm System) which drove the magnetic stirrers and kept the suspensions within 1°C of the desired temperature. After selected time periods, each vial was removed from the block and centrifuged. The caps were then opened, and the supernatant fluid was drawn through a stainless steel needle into a plastic syringe. A membrane filter (Millipore, 13-mm diam., GC, 0.22 μm pores) 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 analyses. 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 reaction vial with the jet of SLF from the syringe. The reaction vial was then capped, vortexed to re-suspend all the particulates and replaced in the heating block. At the end of each dissolution trial, the residual sample was dissolved in 5.00 ml of

warm concentrated nitric acid, diluted with water to the concentration range most suitable for the analytical method, and analyzed.

URANIUM ANALYSES

Prior to dissolution, the solid samples were analyzed for uranium and other metals by X-ray fluorometry. The filtrates from the dissolution trials were analyzed for uranium by two methods: direct fluorometry (DFL) and X-ray fluorometry (XRF). Some of the solutions of residue remaining at the end of the dissolution trials were also analyzed by neutron activation analysis (NAA).

The direct fluorometric method was essentially that described as Method A of ASTM procedure D2907-75.¹¹ Solutions were analyzed by this method at the Hanford Engineering Development Laboratory of the Westinghouse Corporation, Richland, Washington, and the sensitivity was about 1 ppb uranium.

XRF measurements were made with a commercial spectrometer (Kevex, Model 0810) using a tungsten tube-excited secondary source. Solid samples were simply packaged between sheets of polypropylene and mounted in a 2" x 2" slide holder for measurement. The XRF method for uranium in aqueous solutions was developed for this study in order to check values obtained by direct fluorometry. Uranium was extracted from the aqueous solution into hexone (methyl isobutyl ketone) by Method C of ASTM procedure D2907-75, scaled up in volume by a factor of 7. A portion of the resulting extract was then concentrated and finally deposited on a filter disc suitable for XRF analysis. The method consisted of adding 3.50 ml of aqueous sample together with 1.00 ml of concentrated nitric acid to a 50-ml plastic centrifuge tube with a screw cap. A solution of 0.2N potassium permanganate was then added drop-wise until the solution was pink in order to insure oxidation of any uranium to the hexavalent state. Excess permanganate was chemically reduced by drop-wise addition of 0.1 N hydroxylamine hydrochloride. A 28.0-ml portion of tetrapropylammonium hydroxide/salting solution¹⁰ and 14.0-ml of hexone were then added to the centrifuge tube, and the contents were vigorously agitated on a vortex mixer. A 12.0-ml portion of the hexone solution was concentrated by evaporation in a reaction vial at 60°C under a stream of dry nitrogen gas and the residual liquid was dried on a 10-mm diameter disc of filter paper (Whatman 41) with the aid of a heat lamp. The filter disc was then mounted between

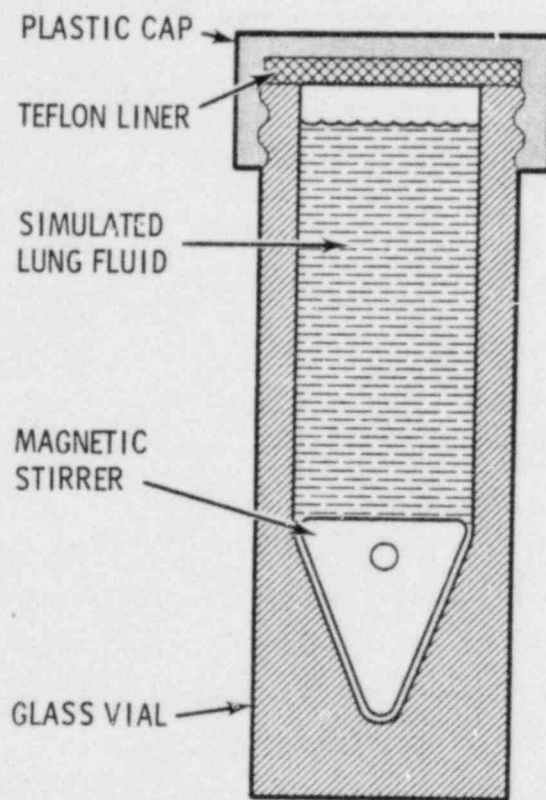


FIGURE 2. Cross Section of Dissolution Chamber for Dust Samples

sheets of polypropylene film in a 2" x 2" slide holder for measurement on the XRF spectrometer. Using standard uranium solutions for calibration, the recovery factor for uranium was 90.1% and the sensitivity was 0.05 μg .

Neutron activation analysis was conducted by drying a sample in the bottom of a plastic vial, irradiating it for 60 minutes with the $1.0 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ flux of neutrons from a ^{252}Cf - ^{235}U source. After a 10-minute delay period, the gamma rays from ^{239}U were counted for 30 minutes using a Ge(Li) detector with NaI(Tl) anticoincidence shield and a pulse-height analyzer. Using standard uranium solutions for calibration, the sensitivity was 0.005 μg .

EVALUATION OF DISSOLUTION HALF-TIMES

Dissolution theory indicates that the fraction of a pure sample remaining undissolved should decrease exponentially with time, unless the particle size range is very broad.¹² Since the samples were expected to contain more than one uranium component with differing dissolution half-times, the data were expected to fit an equation of the form:

$$F = f_1 \exp(-0.693t/T_1) + f_2 \exp(-0.693t/T_2) + \dots + f_n \exp(-0.693t/T_n)$$

where F is the fraction of total uranium remaining undissolved after time t , and the f_j is the initial weight fractions of uranium components in the sample with dissolution half-times t_j . 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. When both DFL and XRF analyses of the dissolved uranium were conducted, the average of the reported values was used for calculating F . Preliminary values of f_1 and T_1 were obtained by graphical analysis of the data, and these were then used as starting values in an iterative computer program (Subroutine NREG from the Madison Academic Computing Center) to obtain the best fit to data by regression analysis.

RESULTS

SAMPLE COLLECTION AND ANALYTICAL DATA

A record was kept of the amounts of dust collected during various intervals of the sampling period along with estimates of the time the wind was blowing from the plant towards the stations. Table 2 shows these data for sample RD11.

TABLE 2. Collection Data for Sample RD11

	<u>Collection*</u> <u>Time</u>	<u>Time with Wind**</u> <u>from Plant</u>	<u>Weight</u> <u>Collected</u>
Sept. 06-09	2.73 d	0.42 d	50.7 mg
" 09-12	2.06	1.87	44.9
" 12-14	1.75	0.25	32.7
" 7-20	2.76	1.04	48.5
" 20-24	3.34	0.71	45.8
" 24-27	2.66	1.29	21.7
" 27-30	2.98	2.45	41.6
" 03-Oct. 03	<u>2.94</u>	<u>1.58</u>	<u>183.1</u>
Sum	21.22	9.61	469.

*Actual time that the sampling pumps were running.

**Estimated time when the wind was from the south to southeast.

Dust forming sample ND11 was not weighed until the entire sample of 302.2 mg had been collected. Sample RD02 was collected for 2.68 days during the period from September 14 to 17. The wind was from the plant, i.e., north to northwest, during all of that time, and a total of 140.8 mg was collected.

The XRF analyses for the solid samples are shown in Table 3. The most outstanding differences in their compositions are the large concentrations of calcium and uranium in sample RD02 and the large amount of lead in sample RD11.

DISSOLUTION BEHAVIOR OF THE SAMPLES

Three dissolution trials were carried out with portions of sample RD11, two trials were carried out with portions of sample ND11, and one trial was carried out with a portion of sample RD02. Different size portions were used in trials with the same sample in order to study the effect of this factor on the dissolution rate. The portion weights and their total uranium contents and concentrations are listed in Table 4.

TABLE 3. XRF Analyses of the Solid Samples

<u>Element</u>	<u>ND11</u>	<u>RD11</u>	<u>RD02</u>
Cl (%)	0.42±.06	<0.14	<0.18
K (%)	.80±.06	0.86±.07	0.50±.06
Cs (%)	3.5±.2	3.6 ± .3	16±1
Ti (%)	.16±.02	.24±.02	.09±.01
Fe (%)	1.16±.08	2.34±.2	1.18±.08
Cr (ppm)	94±11	144±16	81±14
Mn (ppm)	334±25	397±30	481±37
Ni (ppm)	57±5	113±9	45±6
Cu (ppm)	82±6	431±30	175±13
Zn (ppm)	409±29	999±70	824±58
Ga (ppm)	3±1	6±3	<6
Hg (ppm)	<8	16±6	<13
Se (ppm)	<1.3	31±2	<3
Pb (ppm)	256±18	3217±225	990±70
As (ppm)	16±2	<12	95±9
Br (ppm)	92±7	489±34	175±13
Rb (ppm)	18±3	33±3	<20
U (ppm)	429±30	410±29	5375±376
Sr (ppm)	109±8	184±13	126±9
Y (ppm)	15±1	30±3	22±2
Zn (ppm)	128±9	107±8	124±9

TABLE 4. Specifications of Sample Portions

	<u>Portion Wt.</u>	<u>Uranium Wt.</u>	<u>Uranium Conc.</u>
RD11 (total)	0.4690 g	--	--
RD11-1	.2247	98.3 μ g	438 (410) ppm
RD11-2	.0700	42.6	608
RD11-3	.0252	12.4	494
ND11 (total)	0.3022 g	--	--
ND11-1	.1410	87.4 μ g	620 (429) ppm
ND11-2	.0584	39.2	672
RD02 (total)	0.1408 g	--	--
RD02-1	.0600	386.0 μ g	6433 (5375) ppm

The weight of uranium in each portion was calculated by adding up the amounts of uranium dissolved during the dissolution time increments and the amount of uranium in the undissolved residue. These values, together with the fractions of undissolved uranium in the portions at various times are shown in Tables 5 to 10. The uranium concentrations shown in parentheses in Table 4 were obtained by XRF analysis of the solid sample before dissolution.

Graphs of the dissolution data are shown in Figures 3 to 5 and indicate that each portion contained several uranium components with different dissolution half-times. This was confirmed by allowing a computer to fit the data to equations of the form:

$$F = f_1 \exp (-0.693t/T_1) + f_2 \exp (-0.693t/T_2) + \dots + f_n \exp (-0.693t/T_n).$$

In each case, an equation with three exponential terms fits the data within their experimental error. Both two- and four-term equations fit less well. Values of the parameters for optimum fit are listed in Table 11. The 95% confidence intervals for these values are presented in Table 12.

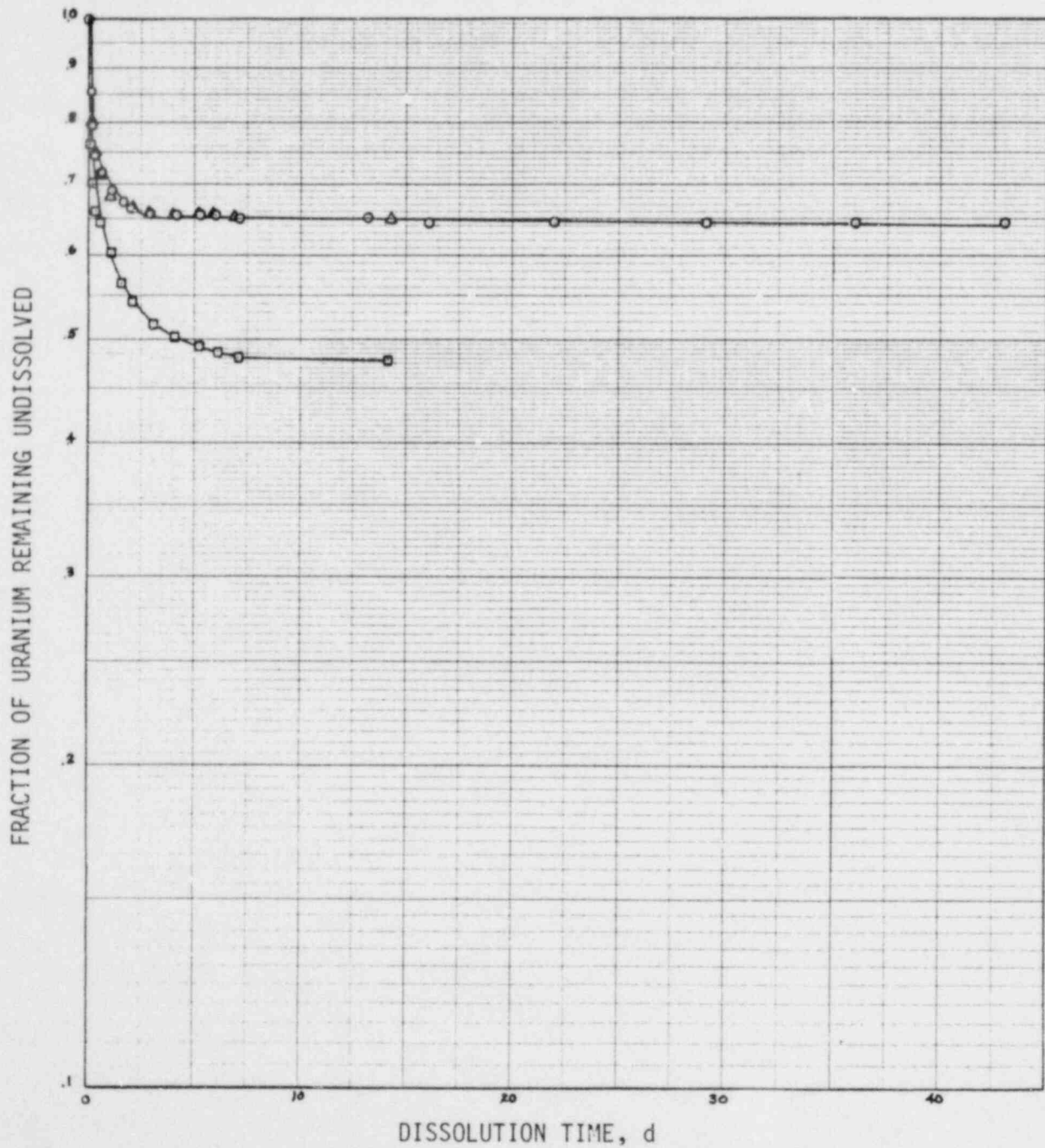


FIGURE 3. Dissolution of Portions RD11-1 (○), RD11-2 (△) and RD11-3 (□)

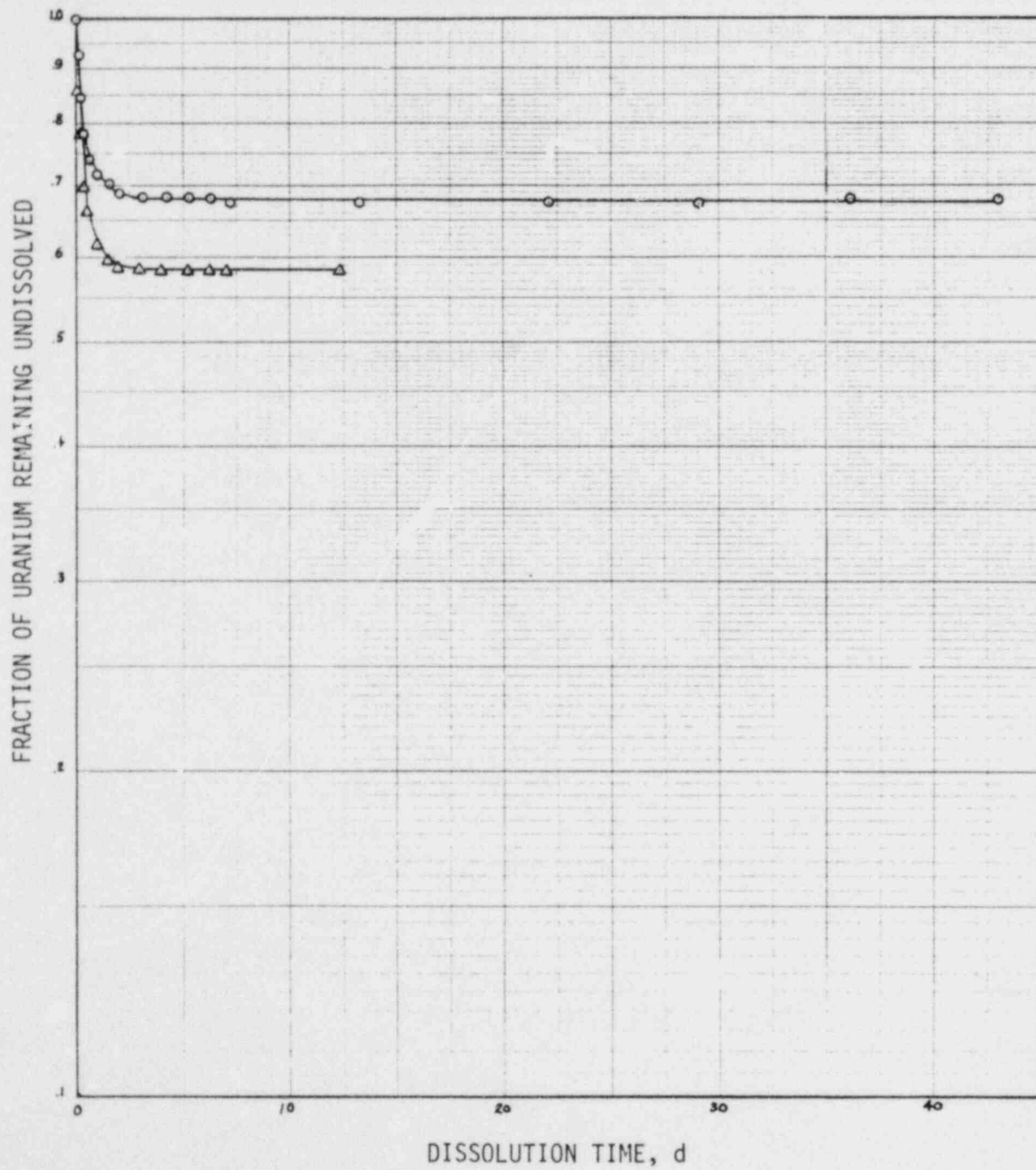


FIGURE 4. Dissolution of Portions ND11-1 (●) and ND11-2 (▲)

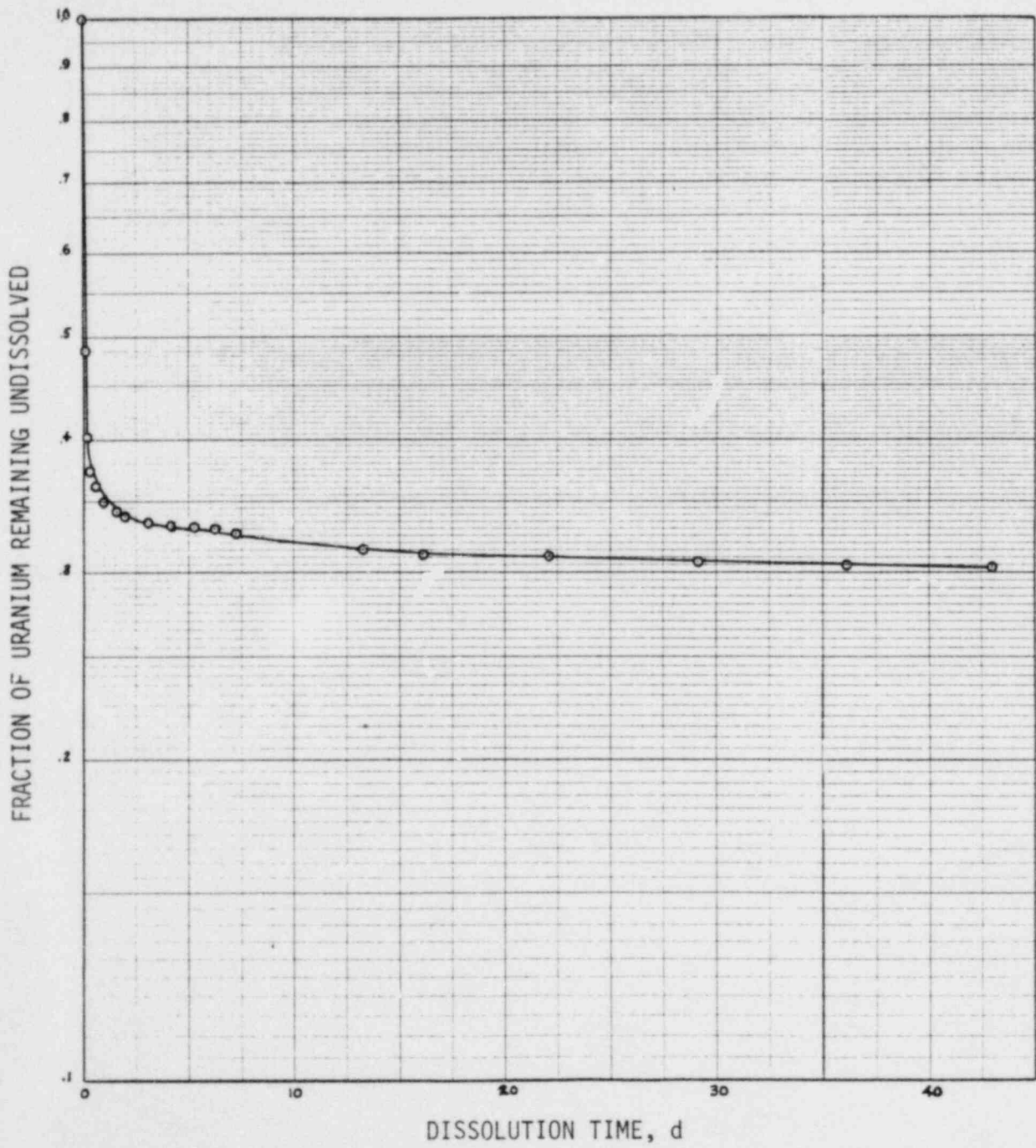


FIGURE 5. Dissolution of Portion RD02-1

TABLE 5. Incremental Amounts of Uranium Dissolved and Fraction of Total Uranium Remaining Undissolved During Dissolution of Sample RD11-1

<u>Time</u>	<u>Ud (XRF)</u>	<u>Ud (NAA)</u>	<u>Ud (DFL)</u>	<u>$\bar{U}d$</u>	<u>F</u>
0.00 d	--	--	--	--	1.000
0.11	13.87	--	14.55	14.21	.855
0.20	6.58	--	5.61	6.10	.793
0.35	4.38	--	5.06	4.72	.745
0.56	3.23	--	2.12	2.68	.718
1.02	2.44	--	2.72	2.58	.692
1.56	1.40	--	2.16	1.78	.673
2.02	1.02	--	0.87	0.95	.664
3.06	0.74	--	0.66	0.70	.657
4.23	0.19	--	0.23	0.21	.655
5.23	<0.04	--	0.07	0.04	.654
6.23	0.16	--	0.22	0.22	.652
7.23	0.15	--	0.15	0.15	.650
13.23	0.23	--	0.35	0.34	.647
16.06	--	--	0.25	0.25	.644
22.03	--	--	0.05	0.09	.644
29.18	--	--	0.01	0.03	.644
36.11	--	--	0.01	0.01	.643
43.03	--	--	0.02	0.02	.643
Residue	63.5	66.0	58.0	<u>63.30</u>	

Total U in sample = 98.32 μ g

TABLE 6. Incremental Amounts of Uranium Dissolved and Fraction of Total Uranium Remaining Undissolved During Dissolution of Sample RD11-2

<u>Time</u>	<u>Ud (XRF)</u>	<u>Ud (DFL)</u>	<u>$\bar{U}d$</u>	<u>F</u>
0.00 d	--	--	--	1.000
0.09	10.42	6.59	8.51	.800
0.18	2.10	1.87	1.99	.753
0.34	1.67	0.36	1.02	.729
0.51	0.72	0.73	0.73	.712
1.02	0.82	1.90	1.36	.580
1.51	0.83	0.47	0.67	.664
2.02	--	0.28	0.28	.658
3.03	--	0.13	0.13	.655
4.01	--	0.05	0.05	.654
5.23	--	0.01	0.01	.653
6.06	--	0.01	0.01	.653
7.04	--	0.06	0.06	.652
14.27	--	0.06	0.06	.650
Residue	27.67		<u>27.67</u>	

Total U in sample = 42.55

TABLE 7. Incremental Amounts of Uranium Dissolved and Fraction of Total Uranium Remaining Undissolved During Dissolution of Sample RD11-3

<u>Time</u>	<u>Ud (XRF)</u>	<u>Ud (DFL)</u>	<u>$\bar{U}d$</u>	<u>F</u>
0.00 d	--	--	--	1.000
0.10	3.13	2.75	2.94	.764
0.19	.94	.62	.78	.701
0.35	.62	.40	.51	.660
0.52	.25	.15	.19	.645
1.03	.50	.64	.56	.600
1.52	.47	.39	.43	.565
2.04	.30	.24	.27	.543
3.04	.31	.30	.30	.519
4.02	--	.22	.22	.502
5.24	--	.09	.09	.494
6.07	--	.09	.09	.487
7.05	--	.06	.06	.482
14.30	--	.06	.06	.477
Residue	5.94		<u>5.94</u>	

Total U in sample = 12.44 μ g

TABLE 8. Incremental Amounts of Uranium Dissolved and Fraction of Total Uranium Remaining Undissolved During Dissolution of Sample ND11-1

<u>Time</u>	<u>Ud (XRF)</u>	<u>Ud (NAA)</u>	<u>Ud (DFL)</u>	<u>$\bar{U}d$</u>	<u>F</u>
0.00 d	--	--	--	--	1.000
0.10	5.83 μ g	--	7.10 μ g	6.47 μ g	.926
0.19	7.68	--	6.40	7.04	.845
0.34	5.83	--	5.40	5.62	.781
0.55	3.41	--	3.70	3.56	.740
1.01	2.76	--	1.85	2.31	.714
1.55	1.20	--	1.05	1.12	.701
2.01	1.42	--	1.10	1.26	.687
3.05	0.36	--	0.39	0.38	.682
4.22	--	--	0.10	0.10	.681
5.22	--	--	0.04	0.04	.681
6.22	--	--	0.05	0.05	.680
7.22	--	--	0.41	0.43	.676
13.22	--	--	0.06	0.06	.675
22.02	--	--	0.19	0.17	.673
29.10	--	--	0.05	0.05	.672
36.10	--	--	0.12	0.12	.671
43.03	--	--	0.06	0.06	.670
Residue	65.5	56.0	54.2	<u>58.57</u>	

Total U in sample = 87.41 μ g

TABLE 9. Incremental Amounts of Uranium Dissolved and Fraction of Total Uranium Remaining Undissolved During Dissolution of Sample ND11-2

<u>Time</u>	<u>Ud (XRF)</u>	<u>Ud (DFL)</u>	<u>$\bar{U}d$</u>	<u>F</u>
0.00 d	--	--	--	1.000
0.08	6.38	4.51	5.45	.861
0.17	3.39	2.72	3.06	.783
0.33	4.84	1.74	3.29	.699
0.50	1.60	1.24	1.42	.663
1.00	2.53	0.97	1.75	.619
1.50	1.28	0.42	0.85	.596
2.01	0.37	0.36	0.36	.587
3.02	--	0.07	0.07	.585
4.00	--	0.02	0.02	.585
5.22	--	0.08	0.08	.583
6.05	--	0.00	0.00	.583
7.02	--	0.03	0.05	.582
14.30	--	0.01	0.01	.582
Residue	22.83		<u>22.83</u>	

Total U in sample = 39.24 μ g

TABLE 10. Incremental Amounts of Uranium Dissolved and Fraction of Total Uranium Remaining Undissolved During Dissolution of Sample RD02-1

<u>Time</u>	<u>Ud (XRF)</u>	<u>Ud (NAA)</u>	<u>Ud (DFL)</u>	<u>$\bar{U}d$</u>	<u>F</u>
0.00 d	--	--	--	--	1.000
.13	174.00	--	223.00	198.50	.486
.21	31.14	--	33.75	32.44	.402
.36	12.01	--	9.45	10.73	.374
.57	5.71	--	3.55	4.63	.361
1.03	4.58	--	4.70	4.64	.350
1.57	2.78	--	2.75	2.77	.343
2.03	1.78	--	1.75	1.76	.338
3.07	1.72	--	1.70	1.71	.334
4.24	0.57	--	0.90	0.73	.332
5.24	0.37	--	0.39	0.38	.331
6.24	0.32	--	0.38	0.35	.330
7.24	3.54	--	2.88	3.20	.322
13.24	2.44	--	2.55	2.49	.315
16.06	1.15	--	1.15	1.15	.312
22.04	0.37	--	0.38	0.38	.311
29.20	1.86	--	1.85	1.85	.307
36.12	--	--	0.73	0.73	.305
43.03	--	--	0.18	0.18	.304
Residue	128	115	104	<u>115.7</u>	

Total U in sample = 386.0 μ g

TABLE 11. Dissolution Parameters of Uranium Compounds in the Sample Portions

Portion	f_1, T_1	f_2, T_2	f_3, T_3
RD11-1	0.24, 0.09d	0.11, 0.69d	0.65, 1861d
RD11-2	0.23, 0.04d	0.12, 0.45d	0.65, 1721d
RD11-3	0.30, 0.05d	0.21, 1.07d	0.49, 375d
ND11-1	0.28, 0.18d	0.04, 1.53d	0.68, 3082d
ND11-2	0.24, 0.09d	0.17, 0.41d	0.59, 3855d
RD02-1	0.63, 0.05d	0.05, 1.60d	0.32, 396d

TABLE 12. 95% Confidence Intervals for the Dissolution Parameters

Portion	Intervals	
RD11-1	$f_1 = 0.22 - 0.25,$ $f_2 = 0.09 - 0.13,$ $f_3 = 0.649 - 0.654,$	$T_1 = 0.08 - 0.10d$ $T_2 = 0.59 - 0.83d$ $T_3 = 1292 - 3325d$
RD11-2	$f_1 = 0.21 - 0.23$ $f_2 = 0.12 - 0.13$ $f_3 = 0.652 - 0.656$	$T_1 = 0.032 - 0.037d$ $T_2 = 0.41 - 0.49d$ $T_3 = 855 - 142,622d$
RD11-3	$f_1 = 0.29 - 0.30$ $f_2 = 0.19 - 0.22$ $f_3 = 0.48 - 0.50$	$T_1 = 0.05 - 0.06$ $T_2 = 0.9 - 1.1$ $T_3 = 195 - 4551$
ND11-1	$f_1 = 0.24 - 0.32$ $f_2 = 0.00 - 0.10$ $f_3 = 0.66 - 0.69$	$T_1 = 0.15 - 0.22d$ $T_2 = 0.65 - 4.3d$ $T_3 = 750 - \infty$
ND11-2	$f_1 = 0.20 - 0.28$ $f_2 = 0.13 - 0.22$ $f_3 = 0.58 - 0.59$	$T_1 = 0.08 - 0.10d$ $T_2 = 0.33 - 0.53d$ $T_3 = 538 - \infty$
RD02-1	$f_1 = 0.62 - 0.64$ $f_2 = 0.03 - 0.06$ $f_3 = 0.32 - 0.33$	$T_1 = 0.05 - 0.06d$ $T_2 = 1.1 - 3.4d$ $T_3 = 268 - 761d$

SOLUBILITY CLASSIFICATIONS

Solubility classifications of the samples were based on the weight fractions and dissolution half-times of the uranium components. Since each sample contained two components in the D category of the ICRP Task Group Lung model, these were combined to show the total weight fraction of uranium in this category. Average values of replicate determinations were calculated to give best estimates of the classifications. The results are listed in Table 13.

TABLE 13. Uranium Solubility Classifications for Dust Collected Near the Allied Plant

<u>Sample</u>	<u>U Content</u>	<u>Classification</u>
RD11	98.2 μg	0.35D, 0.65Y
	43.0	0.35D, 0.65Y
	12.3	0.51D, 0.49Y
		AVE = 0.40D, 0.60Y
ND11	87.4 μg	0.32D, 0.68Y
	39.2	0.41D, 0.59Y
		AVE = 0.37D, 0.63Y
RD02	385.6 μg	0.68D, 0.32Y

DISCUSSION

Interpretation of the dissolution behavior of uranium from an environmental sample presents special complications. Not only can the uranium be expected to occur in several chemical forms, but the sample will usually contain foreign debris such as carbon soot, soil, and bacteria. All of these may adsorb dissolved uranium ions and thus decrease the apparent dissolution rate of uranium from the sample. On the other hand, the dissolution rates may be enhanced by metabolic products of bacterial growth or inorganic ions that rapidly form soluble uranium complexes.

The above-mentioned factors could not be examined extensively within the scope of this study, but the faster dissolution rates observed in the smaller portions, e.g., RD11-3 and ND11-2, are consistent with the possibility that adsorption of dissolved uranium decreased the dissolution rate of uranium from the larger samples. If adsorption of uranium was involved, the amount adsorbed, U_a , would be expected to increase with both the portion weight, W , and the concentration of dissolved uranium, $[U_d]$, according to an equation of the type¹³:

$$U_a = kW [U_d]^m$$

where k and m are positive constants. Since the same replacement schedules and volumes for the exposed SLF were used in all cases, both $[U_d]$ and W are greater in the larger samples, and more adsorption would be expected. Adsorbed uranium may dissolve more slowly than the original uranium compounds or the adsorption sites may simply act as a solid reservoir for the uranium, delaying its removal by filtration. In either case, the apparent dissolution rate of the uranium would be decreased.

Although bacterial growth was not visible in the dissolving suspensions at any time, pretreatment of the samples with ethylene oxide gas at 1 atmosphere pressure for 12 hours would have insured sterilization.

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ACKNOWLEDGMENTS

The cooperation and assistance of the staff of the Allied Chemical Corporation, particularly J. H. Thomas, plant manager, and R. W. Yates, health physicist, are gratefully acknowledged. Staff of the Hanford Engineering Development Laboratory, Westinghouse Electric Corporation, were of considerable help in performing the fluorometric uranium analyses. The assistance of several Battelle staff members, R. W. Sanders, C. L. Wilkerson, and particularly C. Veverka, in collecting and analyzing the samples is also greatly appreciated.

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