

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

1

LA-UR--84-2698

DE84 016784

NOTICE
PORTIONS OF THIS REPORT ARE REPRODUCIBLE
It has been reproduced from the best available copy to permit the broadest possible availability.

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

CONF-841016--2

TITLE DIFFERENCES IN IN VITRO DISSOLUTION PROPERTIES OF SETTLED AND AIRBORNE URANIUM MATERIAL

AUTHOR(S): Ronald C. Scripsick, Kevin C. Crist, Marvin I. Tillery, and Sidney C. Soderholm

SUBMITTED TO: Proceedings of International Conference on Occupational Radiation Safety in Mining, October 1984, Toronto, Canada

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

By acceptance of this article the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

1984 10 16 11:11 AM

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DIFFERENCES IN IN VITRO DISSOLUTION PROPERTIES OF
SETTLED AND AIRBORNE URANIUM MATERIAL*

RONALD C. SCRIBSICK
KEVIN C. CRIST*
MARVIN I. TILLERY
SIDNEY C. SODERHOLM

Los Alamos National Laboratory
University of California
Los Alamos, New Mexico USA

ABSTRACT

The dissolution behavior of settled and airborne uranium material produced by firing of depleted uranium munitions was studied using an in vitro dissolution technique. Differences in the composition of bulk and respirable fraction samples of these materials were observed. Dissolution analysis results suggest that under some conditions a rapidly dissolving uranium fraction may be formed. This fraction may play an important role in determining hazard potential associated with inhalation exposure to uranium materials. The fact that a larger rapidly dissolving fraction was observed in the airborne material than in the settled material indicates that dissolution analysis should be performed on appropriate size fraction samples.

INTRODUCTION

The importance of in vivo dissolution behavior of uranium materials found at uranium mines and mills has been described.^{1,2,3} These studies describe the large variability associated with the dissolution properties of "yellowcake" materials from various uranium mills and demonstrate the usefulness of in vitro dissolution analysis techniques in assessing dissolution behavior. In general, in vivo dissolution behavior has been found to be dependent upon a material's physicochemical form.⁴ In vitro dissolution studies have also been carried out on uranium materials derived from test firing of depleted uranium (DU) penetrator munitions. The complete results of this study are reported elsewhere.⁵ The object of this report is to focus on certain results of the study which indicate that dissolution properties of the uranium materials can be dependent upon the size fraction studied. This result may be of importance in conducting in vitro dissolution analysis of uranium materials found at uranium mines and mills.

MATERIALS AND METHODS

Study Materials

Two DU study materials collected from an enclosed test bunker were provided by the United States Air Force (USAF). Table 1 gives a description of each of these study materials. The test bunker at which the study materials were collected is used for test firings of various DU penetrator munitions. One of the samples (S682-2) was collected as a core sample of the bunker material into which the penetrator is fired. The other (S682-1) was collected by the bunker air cleaning system. The core and air sample materials contained ~10 per cent and ~20 per cent uranium by weight.

TABLE 1: DEPLETED URANIUM STUDY MATERIALS

<u>Sample No.</u>	<u>Treatment</u>
S682-2	Core Sample (settled)
S682-1	Air Sample (airborne)

Sample Generation

Each bulk study material was sieved and the portion passing a 400 mesh (38 μ m mesh size) screen was collected. An aliquot of the sieved material was pressed into a specially made thimble which was mounted on a Wright dust feed⁶ aerosol generator. The dust feed operates by rotating a sample plug against a radially positioned blade that is continually swept by a jet of clean air which suspends the material scraped from the plug. The output of this generator was conducted to a horizontal elutriator (see Fig. 1) operated to pass an aerosol that meets the British Medical Research Council criteria⁷ as being the respirable fraction of the challenge aerosol. Sets of respirable fraction samples representing each study material were collected on 5 μ m pore size, 25 mm diameter Millipore membrane filters. These samples were used in the dissolution experiments.

Dissolution Analysis

Prior to subjecting the respirable fraction samples to dissolution analysis, the mass of uranium (Mg) on each filter was determined using a gross gamma radiometric technique. The technique

*Work performed at the Los Alamos National Laboratory operated under the auspices of the US Department of Energy, Contract No. W-7405-ENG-36.
*Current address: Conoco Inc., Ponca City, Oklahoma, USA

uses a NaI scintillation detector to measure the gamma activity associated with the sample. Standards to relate activity to M_0 were prepared using appropriate laboratory study materials.

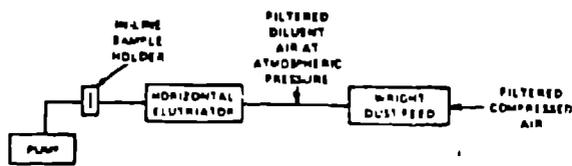


FIGURE 1: RESPIRABLE AEROSOL GENERATION SYSTEM

Once M_0 was determined, the filter containing the respirable fraction uranium sample was sandwiched between two 0.1 μm pore size, 25 mm diameter Nucleopore membrane filters and placed in a dissolution chamber. The chamber (see Figure 2) that was used is a one sided flow system described by Allen⁸ and designed by Moss.⁹

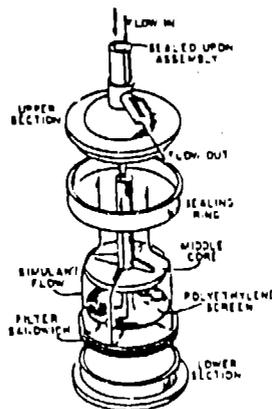


FIGURE 2: THE FLOW DISSOLUTION CHAMBER USED IN THE STUDY

The solvent used in the study was a lung fluid simulant solution described by Moss.¹⁰ The pH of the simulant was maintained at 7.4 ± 0.1 by slowly bubbling 95 per cent O_2 and 5 per cent CO_2 through the simulant as suggested by Moss.¹⁰ The temperature of the simulant was maintained at $37^\circ\text{C} \pm 0.5^\circ\text{C}$ in a water bath. The pH and temperature of the simulant were monitored during the experiment. The simulant was delivered to the dissolution chamber by a peristaltic pump at a flow rate of 1 mL/min. The experiments were operated for at least 30 days.

Simulant passing out of the dissolution chamber was collected at selected times. The samples were collected in polyethylene bags which were heat sealed and placed in pneumatic "rabbits" for automated delayed neutron activation (DNA) analysis.

X-ray Diffraction Analysis

The composition of bulk and respirable fraction samples was determined using x-ray diffraction. The method, which followed the procedure outlined by Klug,¹¹ uses a standard vertical diffractometer with a graphite monochromator and a proportional detector. This technique permits the determination of species and quantity of crystalline materials and can detect the presence of amorphous materials at levels greater than 10-20 per cent by weight. To ascertain the percentage of uranium oxide present as the dioxide, standards were prepared from well characterized, selected UO_2 and U_3O_8 powders. A calibration curve was then drawn from which the results were obtained.

DATA ANALYSIS AND RESULTS

From the DNA data and values of M_0 , estimates of the fraction of remaining uranium dissolved per day (f_d) were calculated as follows for each sample:

$$f_{d,j} = \frac{m_j}{d \left[M_0 - \sum_{k=1}^j \left(\frac{(m_k + m_{k-1})(t_k - t_{k-1})}{2d} \right) \right]} \quad (1)$$

where, m_j and m_k = the mass of uranium in the j th and k th samples respectively, d = duration of sample collection in days, and t_k = elapsed time, in days, to the midpoint of the sample collection period. The results of these calculations were plotted against time for each of the study materials. Curves were fit to these data using a nonlinear least squares fitting routine¹² with the estimated variance of each f_d value weighting the fit. The plots with the fitted curves are shown in Figure 3. These data were fit with a model of the form:

$$f_d = \frac{M(t - d/2) - M(t + d/2)}{d \cdot M(t)} \quad (2)$$

where, $M(t)$ = the mass of uranium remaining at time t which equals

$$M_0 \sum_{i=1}^n f_i \exp(-\lambda_i t), \quad f_i = \text{the } i\text{th dissolution component}$$

components included in the fit, n = the total number of dissolution components, f_i = the mass fraction of the sample associated with the i th dissolution component and λ_i = the dissolution rate constant of the i th dissolution component.¹³

The fitting routine would not converge for $n > 2$ even though a three component ($n = 3$) fit seemed appropriate from inspection of the plots. Consequently, data corresponding to the latter two of the three observed dissolution components was fit with $n = 2$. The results of the curve fitting were used to derive f_i and λ_i values found in Table 2. Characterization of the earliest observed dissolution component was limited to estimates of f_1 (see Table 2) and a lower limit on λ_1 . The value of λ_2 was used as the lower limit of λ_1 .

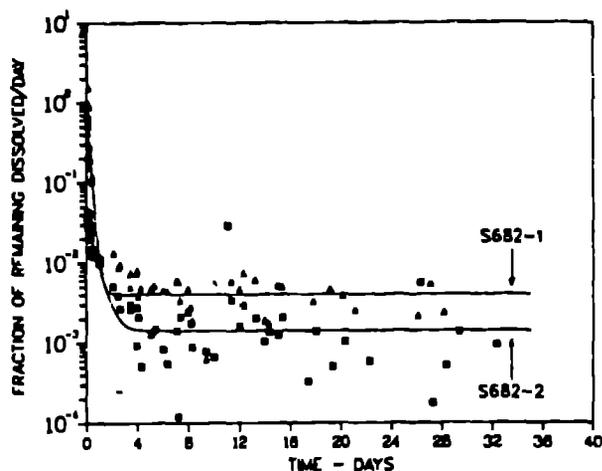


FIGURE 3: PLOT OF DISSOLUTION EXPERIMENT DATA AND FITTED CURVES FOR THE RESPIRABLE FRACTION OF STUDY MATERIALS S682-1 (□) AND S682-2 (Δ)

Dissolution half-times,

$$T_1 = \ln 2 / \lambda_1 \quad (3)$$

were calculated for each value of λ_1 . These values are shown in Table 2.

For sufficiently large t , f_d becomes time independent and takes on the value of λ_3 . The average value of f_d corresponding to long times was computed as a separate estimate of λ_3 . This value of λ_3 was considered to be free of influence from earlier f_d values that affect the estimation of λ_3 by the least squares method mentioned above. Table 3 gives the values of λ_3 obtained by this analytical method. The λ_3 estimates obtained by the two methods agree well. Multiple comparisons analysis performed using the values in Table 3 indicated that there was a significant difference (at the 95 per cent confidence interval) between the λ_3 values associated with the study materials. Table 3 also gives values of T_3 calculated using the values of λ_3 listed in Table 3.

TABLE 3: LONG-TERM PHASE DISSOLUTION PARAMETERS CALCULATED USING AVERAGING TECHNIQUE

Study Material No.	N ^a	λ_3 -Days ⁻¹	T_3 -Days ^c
S682-2	22	$1.5 \times 10^{-3} \pm 3 \times 10^{-4}$	480 ± 85
S682-1	25	$3.8 \times 10^{-3} \pm 4 \times 10^{-4}$	180 ± 20

^aN = number of datapoints associated with analysis
^bValue \pm standard deviation

^c T_3 = dissolution half-time of long-term dissolution component.

TABLE 4: RESULTS OF X-RAY DIFFRACTION ANALYSIS

Study Material No.	Weight Per cent of Uranium Oxide as UO ₂ ^a	
	Respirable Fraction	Bulk
S682-2 (settled)	54 ^b	97
S682-1 (airborne)	18	60

^aRemainders are U₃O₈.

^bThe error in the estimates is < 10 per cent of the respective values.

The results of x-ray diffraction analysis of the bulk and respirable fraction samples indicated that the crystalline uranium in the samples consisted of U₃O₈ and UO₂. Table 4 shows the percentage of the uranium oxide found in the samples as UO₂; the balance of the crystalline uranium material was determined to be U₃O₈. Amorphous material was detected in the respirable fraction of the air sample material (S682-1). The fraction of the sample associated with amorphous material was estimated to be ~20 per cent by weight.

DISCUSSION AND CONCLUSIONS

Differences in Dissolution Behavior

Only ~4 per cent of the respirable fraction of the core sample material (S682-2) was associated

TABLE 2: DISSOLUTION PARAMETERS DERIVED FROM TWO COMPONENT EXPONENTIAL LEAST SQUARES FITS

Study Material No.	N ^a	Initial Dissolution Phase				Long-Term Dissolution Phase		
		First Component		Second Component		Third Component		
		f_1	f_2	λ_2 -Days ⁻¹	T_1 -Days ^c	f_3	λ_3 -Days ⁻¹	T_3 -Days
S682-2	61	0.02 ± 0.0006	0.02 ± 0.002	1.7 ± 0.2	0.41 ± 0.08	0.95 ± 0.002	$1.4 \times 10^{-3} \pm 2.0 \times 10^{-4}$	490 ± 70
S682-1	56	0.12 ± 0.04	0.13 ± 0.01	4.7 ± 0.5	0.14 ± 0.02	0.75 ± 0.03	$4.0 \times 10^{-3} \pm 4.7 \times 10^{-4}$	170 ± 20

^aN = number of data points associated with the analysis.

^bValue \pm standard deviation.

^c T_1 = dissolution half-time of 1st dissolution component.

with initial phase dissolution (see Table 2). In contrast, the respirable fraction of the air sample material studied here (S682-1) and similar samples studied by Glissmeyer¹⁴ had from 11 to 45 per cent of the material associated with initial phase dissolution (see Table 2). This suggests that a larger fraction of material suspended in the air during DU penetrator test firings may be readily available for systemic contamination than would be indicated by the clearance classifications of U₃O₈ and UO₂^{15,16,17} or the results of in vitro studies of laboratory prepared U₃O₈ and UO₂ material.^{17,18} This also indicates that important dissolution behavior differences can exist between size segregated samples from a common source such as the settled and airborne materials studied here.

Eidson¹ attributed the initial phase seen in the dissolution of "yellowcake" samples to the presence of ammonium diuranate, a rapidly dissolving uranium material. The material produced during test firing of penetrators was also observed to contain a rapidly dissolving fraction. This fraction was evident to a greater extent in the air sample material (S682-1) than in the core sample material (S682-2). The air sample material (S682-1) is thought to be made up of particles with low settling velocities relative to those in the core sample material (S682-2). For a given specific gravity, the lower settling velocity material would have a relatively high specific surface area which could explain the large concentration of rapidly dissolving material in the respirable fraction of the air sample material (S682-1). In addition, the fact that ~70 per cent by weight of the respirable fraction sample of study material S682-1 was found to be amorphous and that this amorphous material may contain uranium suggests the possibility that at least a portion of the rapidly dissolving fraction may be rapidly dissolving amorphous uranium compounds. Therefore, rather than chemical character of the material alone accounting for initial phase dissolution as Eidson found for "yellowcake", initial phase dissolution for these materials may be a consequence of the physical character of the material as well as the chemical composition of the material. This study does not resolve which is the more important.

The long-term dissolution half-times (T₃) observed here fall in the range of long-term half-times found by Eidson¹ for similar materials (from 140 days to 500 days). These half-times also agree with the "Y" clearance classifications assigned to U₃O₈ and UO₂.^{15,16,17}

The long-term dissolution half-time associated with the respirable fraction of the airborne study material (S682-1) was found to be significantly higher (at the 95 per cent confidence level) than the long-term dissolution half-time associated with the respirable fraction of the settled study material (S682-2). As discussed above, this difference may be a consequence of the physical character of the material such as the specific surface area as well as its chemical composition.

The fact that significant differences were observed in the dissolution behavior of the study materials highlights the necessity of performing

dissolution analysis on appropriate size fraction samples. Results from dissolution analysis of core sample material (S682-2) may be most useful in assessing exposure to material resuspended during such activities as bunker dismantling. Whereas, results from analysis of air sample material may be most useful in assessing exposure to material suspended during penetrator firings.

Results of in vitro dissolution analysis reported by Eidson¹ on bulk "yellowcake" samples agree with laboratory animal lung clearance data obtained from inhalation studies using samples of the same "yellowcake" materials.¹⁹ This indicates that, for the "yellowcake" materials studied, dissolution analysis results for bulk materials are useful in assessing exposures to suspended materials. Our results demonstrate that this is not always the case and, in general, in vitro dissolution analysis should be performed with appropriate size fraction samples. This is especially important when no in vivo data is available to support in vitro results.

Composition Differences Between Bulk and Respirable Fraction Samples

A significant difference in the UO₂ content between bulk and respirable fraction samples was observed in both study materials (see Table 4). Glissmeyer¹⁴ noticed a similar size segregation. The direction of this segregation; namely, that U₃O₈ is associated with the smaller particle sizes, agrees with data presented by Steckle¹⁸ and Fider.²⁰

This finding again points out the importance of performing dissolution analysis, as well as other analyses, on appropriate size selected samples. Analysis of bulk material or even total suspended particulate samples may result in inaccuracies in prediction of lung clearance rates and/or incorrect associations of dissolution half-times with the physicochemical character of the study material. These inaccuracies and incorrect associations, in addition to being related to differences in the physical character of deposited and study materials, may also be related to chemical differences in these materials.

SUMMARY

Differences in the in vitro dissolution behavior between settled and airborne uranium materials were observed. In addition, differences in the composition of bulk and respirable fraction samples of each of these materials were found. These discoveries indicate the importance of selecting appropriate size fraction samples on which to perform dissolution analysis as well as other analyses used to characterize samples.

ACKNOWLEDGEMENTS

This report is the culmination of the efforts of many individuals whom we thank and acknowledge here. These people include: Jim Cornette of the United States Air Force; Owen Moss of Pacific Northwest Laboratory; George Kanapilly (deceased)

of Lovelace Inhalation Toxicology Research Institute; and from Los Alamos, Marvin Tinkle and other staff of the Nuclear Materials Process Technology group, John O'Rourke of the Physical Metallurgy group, Ernie Gladney, Dan Perrin, Hal Ide, and Bill Moss of the Health and Environmental Chemistry group, Mike Minor of the Research Reactor group, and Dave White and Dick Beckman of the Statistics group. Lloyd Wheat of the Industrial Hygiene group provided technical assistance during aerosol generation, dissolution apparatus design, dissolution analysis, and data reduction. Kevin Burgett, formerly of the Industrial Hygiene group, assisted during the dissolution analysis.

REFERENCES

1. EIDSON, A.F., MEWHINNEY, J.A., "In vitro Solubility of Yellowcake Samples from Four Uranium Mills and the Implications for Bioassay Interpretation", Health Physics 39, p. 893-902, 1980.
2. KALKWARF, D.R., "Solubility Classification of Airborne Products from Uranium Ores and Tailings Piles", Pacific Northwest Laboratory report PNL-2970, Hanford, Washington, 1979.
3. DENNIS, N.A., BLAUER, H.M., KENT, J.E., "Dissolution Fractions and Half Times of Single Source Yellowcake in Simulated Lung Fluids", Health Physics 42, pp. 469-477, 1982.
4. KANAPILLY, G.M., "Alveolar Microenvironment and Its Relationship to the Retention and Transport into Blood of Aerosols Deposited in the Alveoli", Health Physics, 32, pp. 89-100, 1977.
5. SCRIPSICK, R.C., CRIST, K.C., TILLERY, M.I., and SODERHOLM, S.C., "Preliminary Study of Uranium Oxide Dissolution in Simulated Lung Fluid", in preparation, 1984.
6. WRIGHT, B.M., "A New-Feed Mechanism, J. Sci. Instr. 27, 12, 1975.
7. AEROSOL TECHNOLOGY COMMITTEE, "Guide for Respirable Mass Sampling", Amer. Ind. Hyg. Assoc. J. 33, 133, 1970.
8. ALLEN, M.D., BRIANT, J.K., MOSS, O.R., ROSSIGNOL, E.J., MAHBUM, D.D., MORGAN, L.G., RYAN, J.L., AND TURCOTTE, P.P., "Dissolution Characteristics of LMFBR Fuel-Sodium Aerosols", Health Physics, 40, 183, 1981.
9. MOSS, O.R., and KANAPILLY, G.M., "Dissolution of Inhaled Aerosols", in: Generation of Aerosols, ed. Klaus Willeke, Ann Arbor Science Publication, 1980.
10. MOSS, O.R., "Simulants of Lung Intersitial Fluid", Health Physics, 36, pp. 447, 1979.
11. KLUG, H.P. and ALEXANDER, L.E., "X-Ray Diffraction Procedures", Wiley, New York, New York, 1974.
12. TRUSSELL, J.H., "Generalized Least Square Package", Los Alamos Program Library Write-up, GFAA, Los Alamos, New Mexico, October 1979.
13. MERCER, T.T., "ON THE Role of Particle Size in the Dissolution of Lung Burdens", Health Physics 13, pp. 1211-1221, 1967.
14. GLISSMEYER, J.A., MISHIMA, J., "Characterization of Airborne Uranium from Test Firings of XMFF4 Ammunition", Pacific Northwest Laboratory report PNL-2944, Hanford, Washington, 1979.
15. TASK GROUP ON LUNG DYNAMICS, "Deposition and Retention Models for Internal Dosimetry of the Human Respiratory Tract", Health Physics, 12, pp. 173-207, 1966.
16. COOKE, N., HOLD, F.B., "The Solubility of Some Uranium Compounds in Simulated Lung Fluid", Health Physics 27, pp. 69-77, 1974.
17. KALKWARF, D.R., "Solubility Classification of Airborne Uranium Products from LWR-Fuel Plants", Pacific Northwest Laboratory report PNL-3411, Hanford, Washington, 1980.
18. STECKEL, L.M., WEST, C.M., "Characterization of Y-12 Uranium Process Material Correlated with In Vivo Experience", US Atomic Energy Commission report Y-1544-A, 1966.
19. DAMON, E.G., EIDSON, A.F., HAHN, F.F., GRIFFITH, Jr., W.C., and GUILMETTE, R.A., "Comparison of Early Lung Clearance of Yellowcake Aerosols in Rats with In Vitro Dissolution and IR Analysis", Health Physics 46, pp. 859-866, 1984.
20. ELDER, J.C., TINKLE, M.C., "Oxidation of Depleted Uranium Penetrators and Aerosol Dispersal at High Temperatures", Los Alamos National Laboratory report LA-8610-MS, Los Alamos, NM, 1980.