23

ORNL-2519

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0361257 0

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.
UCN-7969 (3 9-77)

A Facsimile Report

Reproduced by
UNITED STATES DEPARTMENT OF ENERGY
Technical Information Center
P. O. Box 62 Oak Ridge, TN 37830

0/325

MASTER

ORNL-2519
Chemistry-Separation Processes
for Plutonium and Uranium

DISSOLUTION OF SINTERED THORIUM-URANIUM OXIDE FUEL IN NITRIC ACID-FLUORIDE SOLUTIONS

W. D. Bond

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

3 4456 0361257 0
MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

ORNL-2519

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

DISSOLUTION OF SINTERED THORIUM--URANIUM OXIDE FUEL IN NITRIC ACID--FLUORIDE SOLUTIONS

W. D. Bond

DATE ISSUED

NOV 14 1958

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ABSTRACT

Boiling 13 M HNO_3--0.04 M NaF appears to be a suitable dissolvent for the 96% ThO_2--4% UO_2 fuel element core material similar to that to be used by Consolidated Edison. Dissolution of unirradiated 1/4-in.-dia pellets was 98% complete in 5.3 hr, producing a final product solution of 8.6 M HNO_3--1 M $Th(NO_3)_4$--0.041 M $UO_2(NO_3)_2$ at an overall average dissolution rate of 3.4 mg/cm^2·min. Extrapolation of the rate data indicates that complete dissolution could be achieved in 6-7 hr. A stepwise procedure with fresh dissolvent would produce faster dissolution rates. The total dissolution time was 1-2 hr for pellets that had been crushed to a powder. Sulfuric, nitric, and hydrofluoric acids and aqua regia were ineffective dissolution agents.

CONTENTS

		Page No.
1.0	INTRODUCTION	4
2.0	RESULTS OF DISSOLUTION TESTS	4
2.1	Fluoride Concentration	4
2.2	Nitric Acid and Thorium Nitrate Concentrations	5
2.3	Dissolvent Volume/Surface Area Ratio	7
2.4	Pellet Pulverization	8
2.5	Alternate Solvents	8
3.0	EXPERIMENTAL DETAILS	15
3.1	Materials and Chemicals	15
3.2	Apparatus	15
3.3	Dissolution Testing Procedures	15
4.0	REFERENCES	17
5.0	APPENDIX	18

1.0 INTRODUCTION

This investigation was performed to find a suitable aqueous dissolvent for ThO_2-UO_2 sintered pellets which are to be used as fuel in power reactors. The study was confined to 96% ThO_2--4% UO_2 pellets which are similar to those to be used in the Consolidated Edison Power Reactor. Further studies will deal with pellets containing other ratios of thorium to uranium. The effect of additives to produce desirable sintering effects will also be studied.

An extensive laboratory investigation was made on nitric acid--sodium fluoride mixtures as a possible dissolvent for this fuel. Previous studies[1-6] have shown the feasibility of dissolving thorium metal and thorium oxide in nitric acid--fluoride mixtures. Dissolution of the fuel by nitric acid--fluoride mixtures is particularly attractive since the fuel could be reprocessed in the same way as thorium metal is now handled in the Thorex process.[7-11]

The author expresses sincere appreciation to G. W. Wilson and his group of the Analytical Chemistry Division who performed all analyses, and to W. E. Clark who made many helpful suggestions throughout the course of the work.

2.0 RESULTS OF DISSOLUTION TESTS

The concentrations of fluoride, nitric acid and thorium nitrate, the initial dissolvent volume/surface-area ratio, and the fine pulverization of the pellets were studied for their effects on the dissolution rate of ThO_2-UO_2.

2.1 Fluoride Concentration

The 3-hr dissolution rates of 96% ThO_2--4% UO_2 pellets were, within experimental error, independent of fluoride concentrations in boiling 13 M HNO_3 over a range of fluoride concentrations from 0.01 M to 0.5 M (Table 1). However, ThF_4 was precipitated with fluoride concentrations of 0.1 M or greater. Thus the fluoride released from pellet dissolution (about 0.20 wt %) should have no effect on the dissolution rate or precipitate formation. Nitric acid containing 0.04 M NaF was chosen as the dissolvent for further study since thorium fluoride does not precipitate with this dissolvent, and the fluoride concentration of this dissolvent is the same as that now used in the Thorex process.

Table 1. Dissolution of 96% ThO_2--4% UO_2 Sintered Pellets in 13 M Nitric Acid--Fluoride Mixtures

Sodium Fluoride Conc, M	Rate,[a] $mg/cm^2 \cdot min$	ThF_4 Precipitation	Pellet Dissolution,[b] %
0.01	5.5	None	98
0.04	5.7	None	93
	6.2	None	87
0.1	5.1	Slight	87
0.5	2.9	Excessive	48
	2.9	Excessive	49
	5.4[c]	Excessive	89

[a]Single pellet tests.

[b]At 90% dissolution, the dissolved thorium concentration is about 0.2 M.

[c]The ThF_4 did not adhere to the sample in this case. This specimen was run in a stainless steel container in which the boil-up rate was higher than in the Teflon pot used for the other two.

2.2 Nitric Acid and Thorium Nitrate Concentrations

Practically speaking, the results indicated that the dissolution rate is acceptable with 13 M HNO_3--0.04 M NaF solutions and that it is markedly decreased by increasing $Th(NO_3)_4$ concentration and/or decreasing acid concentration. Thus, it appears that 13 M HNO_3--0.04 M NaF is a practical dissolvent for this material if the dissolution is not allowed to proceed much farther than when the solution becomes 1 M in $Th(NO_3)_4$ and 8-9 M in HNO_3. The dissolution rate of 96% ThO_2--4% UO_2 pellets in nitric acid containing 0.04 M NaF increased rapidly with increasing nitric acid concentration to a maximum of 11.2 $mg/cm^2 \cdot min$ in 13 M HNO_3. The rate decreased markedly as the thorium nitrate concentration increased (Table 2 and Fig. 1). The change in the dissolution rate with nitric acid is most rapid in the 2-8 M range. By graphical methods (see Appendix) it was shown for this acidity range that the dissolution rate is approximately proportional to the third power of the acid concentration for solutions containing no thorium nitrate and to the fourth power of the acid concentration for solutions containing 0.3 M and 0.9 M

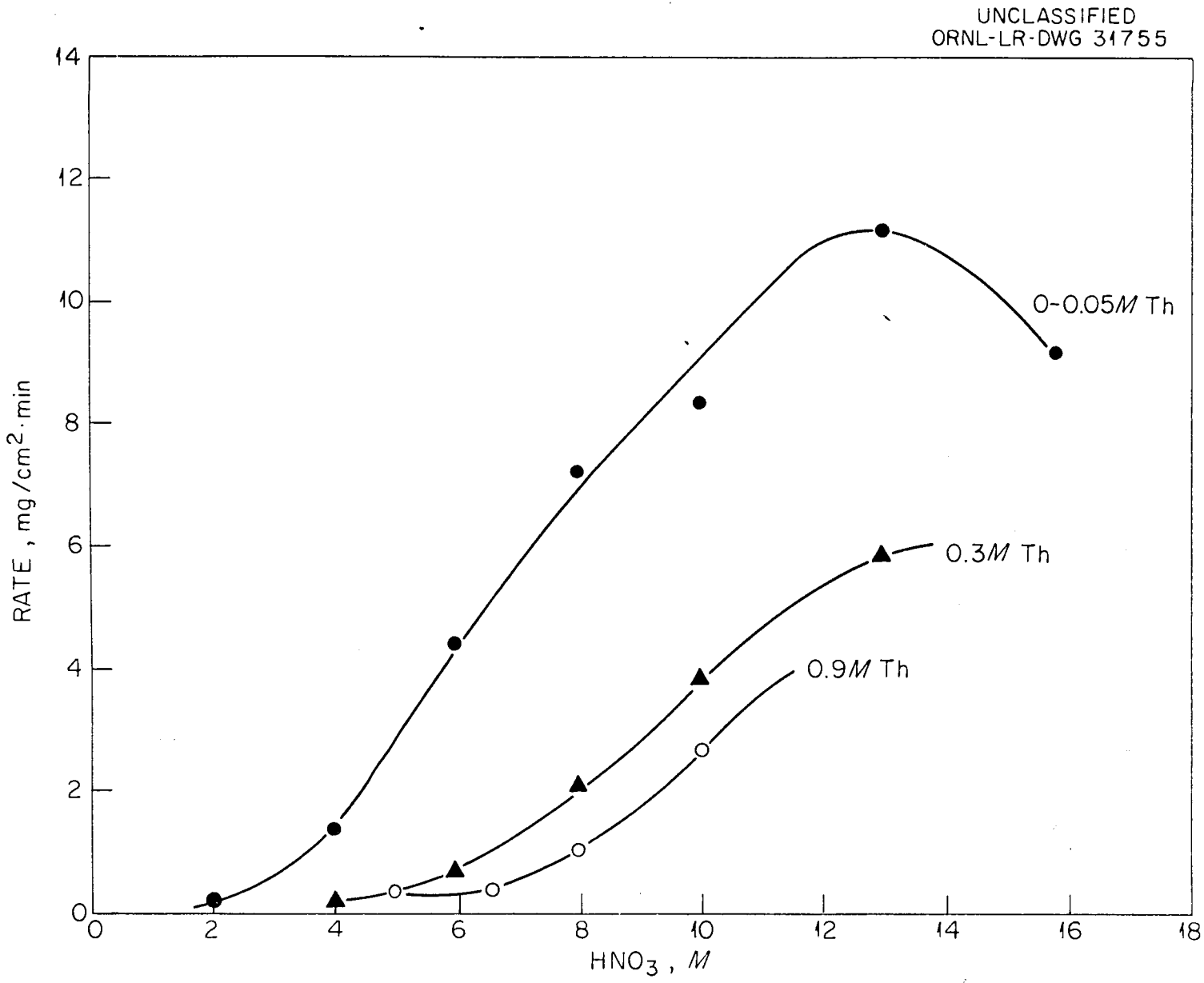

Fig. 1. Rate of dissolution of sintered 96% ThO_2–4% UO_2 pellets in boiling nitric acid containing 0.04M NaF as a function of nitric acid and thorium nitrate concentrations.

$Th(NO_3)_4$. In the region 8-13 M HNO_3 the dissolution rate is approximately proportional to the first power of the nitric acid concentration for all thorium concentrations.

Table 2. Effect of Nitric Acid and Thorium Nitrate Concentrations on Dissolution Rate

HNO_3 M	Instantaneous Dissolution Rate, $mg/cm^2 \cdot min$		
	0 M $Th(NO_3)_4$	0.3 M $Th(NO_3)_4$	0.9 M $Th(NO_3)_4$
2	0.19	0.013	a
3	a	a	0.05
4	1.39	0.17	a
5	a	a	0.38
6	4.45	0.67	a
6.6	a	a	0.36
8	7.20	2.12	1.04
10	8.35	3.84	2.70
13	11.2	4.85	a
15.8	9.15	a	a

[a] Data not taken.

The decrease in dissolution rate with increasing thorium nitrate concentration indicates that thorium is reducing the fluoride below its optimum concentration by the formation of the moderately strong complexes,[12,13] ThF^{+3} and ThF_2^{+2}. Additional studies are needed to develop a procedure for maintaining optimum fluoride concentration.

2.3 Dissolvent Volume/Surface Area Ratio

Since the surface area of the cylindrical pellets rapidly changes as dissolution proceeds, a more practical approach to the problem is to measure the dissolution time required to produce certain desired thorium nitrate and nitric acid concentrations at various extents of pellet dissolution for several initial V/S (dissolvent volume/surface area) ratios. Such a study permits determination of a wide range of

conditions for the dissolution of the pellets. Thorium nitrate and nitric acid concentrations were studied as a function of dissolution time for seven initial V/S ratios which ranged from 0.795 to 6.45 cm and the results plotted (Figs. 2,3). The extent of pellet dissolution and average dissolution rates was calculated from the measured thorium nitrate concentration (Table 3).

A V/S ratio of 3.84 appears to be the best compromise, considering over-all dissolution rate, acid consumption, and extent of pellet dissolution (Fig. 4). At this ratio, pellet dissolution was 98% complete producing a product solution of 8.6 M HNO_3-1 M $Th(NO_3)_4$-0.041 M $UO_2(NO_3)_2$ at an average over-all dissolution rate of 3.4 $mg/cm^2 \cdot min$ (Table 3). Extrapolation of the data rate data indicates that complete dissolution could be achieved in 6-7 hours (Fig. 2). The total dissolution time could be decreased by the use of fresh dissolvent in later stages of the dissolutions. This would eliminate lowered dissolution rates because of low acid and high thorium nitrate concentrations near the end of the dissolution process.

2.4 Pellet Pulverization

Pulverizing the pellets to fine powders ($\sim$1190 μ) prior to dissolution greatly decreased the time required for complete dissolution of the pellets. The powder dissolved about five times as quickly as the uncrushed pellets (Fig. 5).

2.5 Alternate Solvents

Sulfuric acid (4 and 6 M), nitric acid (3, 10, 13, and 15.8 M), hydrofluoric acid (2, 5, 9, and 12 M), hydrochloric acid--nitric acid mixtures (2 M--5 M, 9 M--4 M, and 4 M--12 M), and 6 M H_2SO_4--0.04 M NaF were investigated as possible alternate dissolvents. All measured rates were below 0.60 $mg/cm^2 \cdot min$ (Table 4). These dissolvents therefore are of little value for dissolving this fuel.

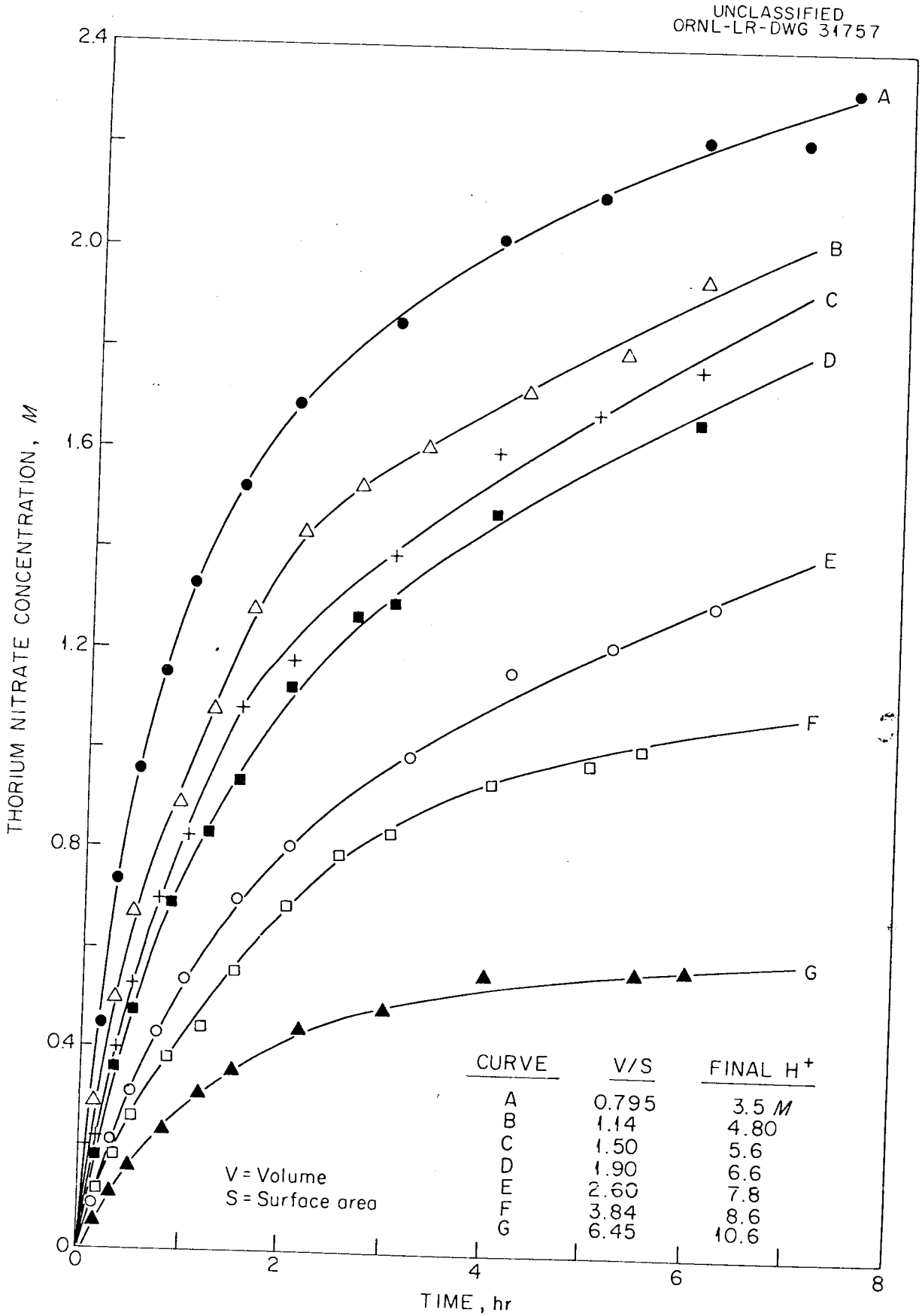

Fig. 2. Thorium nitrate concentration as a function of time in dissolution of sintered 96% ThO_2–4% UO_2 pellets in boiling 13M HNO_3–0.04M NaF. V = initial volume; S = initial surface area.

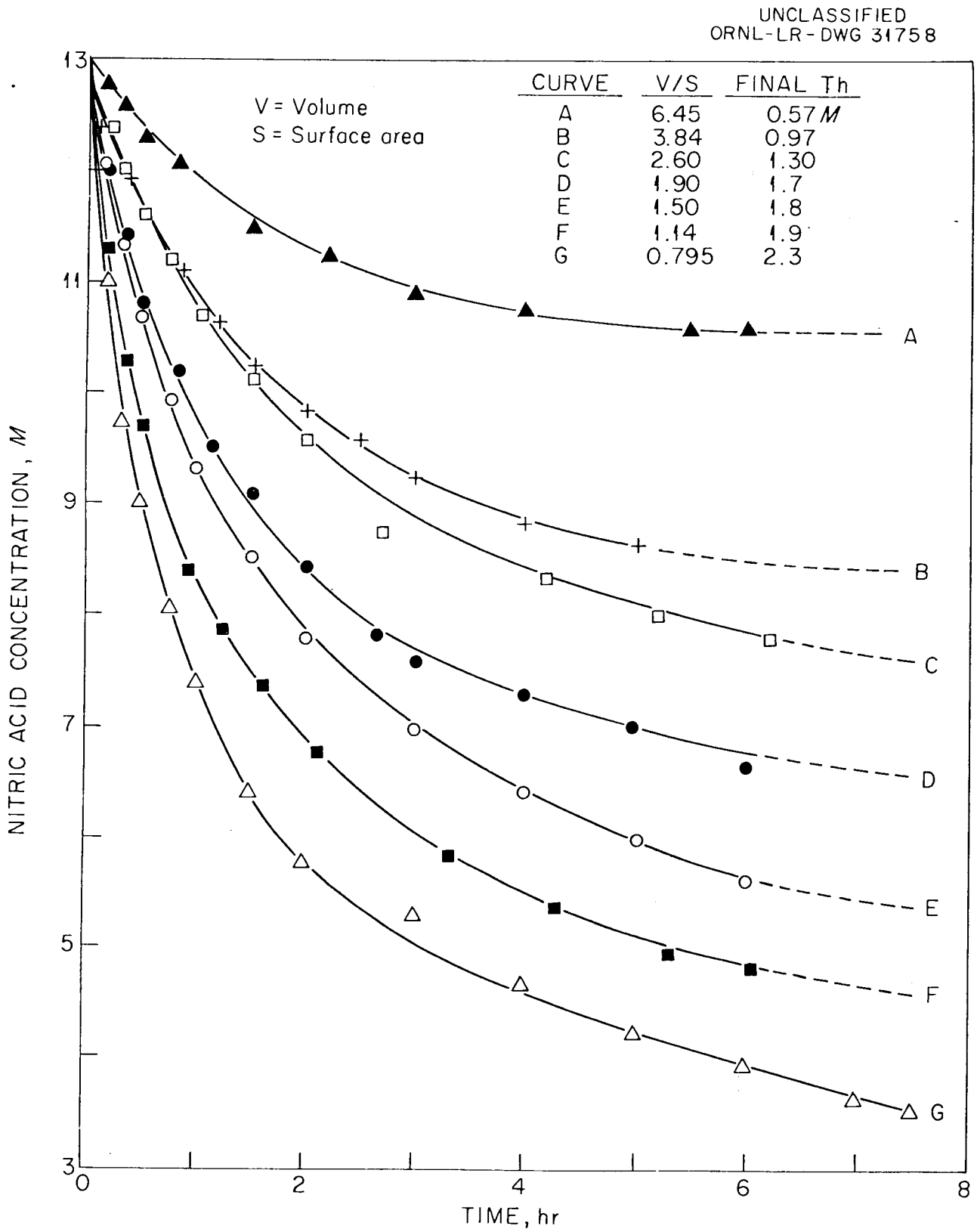

Fig. 3. Nitric acid concentration as a function of time in dissolution of sintered 96% ThO_2–4% UO_2 pellets in boiling 13M HNO_3–0.04M NaF. V = initial volume; S = initial surface area.

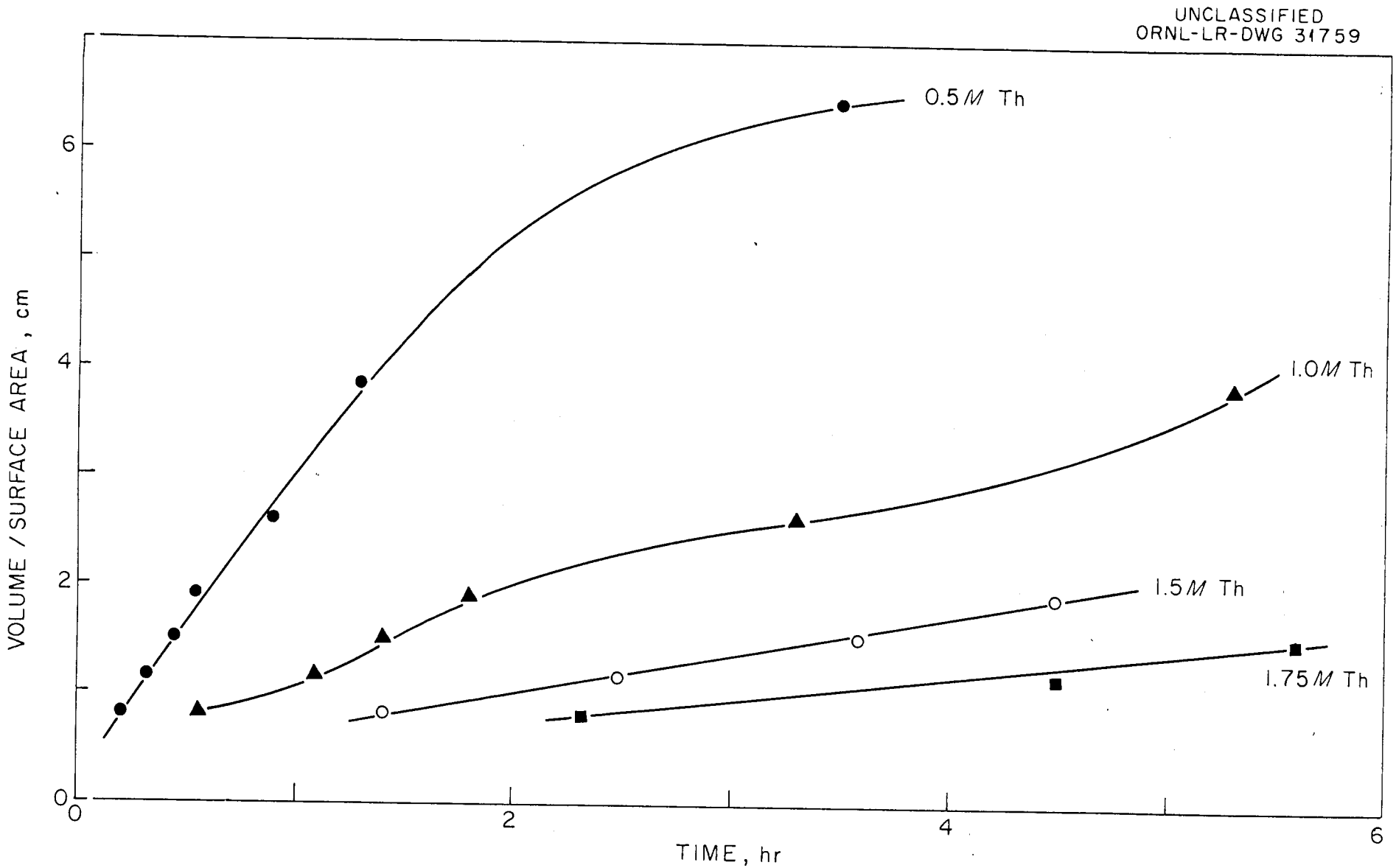

Fig. 4. Initial V/S ratios as a function of time required to produce specific thorium nitrate concentrations in dissolution of sintered 96% ThO_2–4% UO_2 pellets in boiling 13M HNO_3–0.04M NaF.

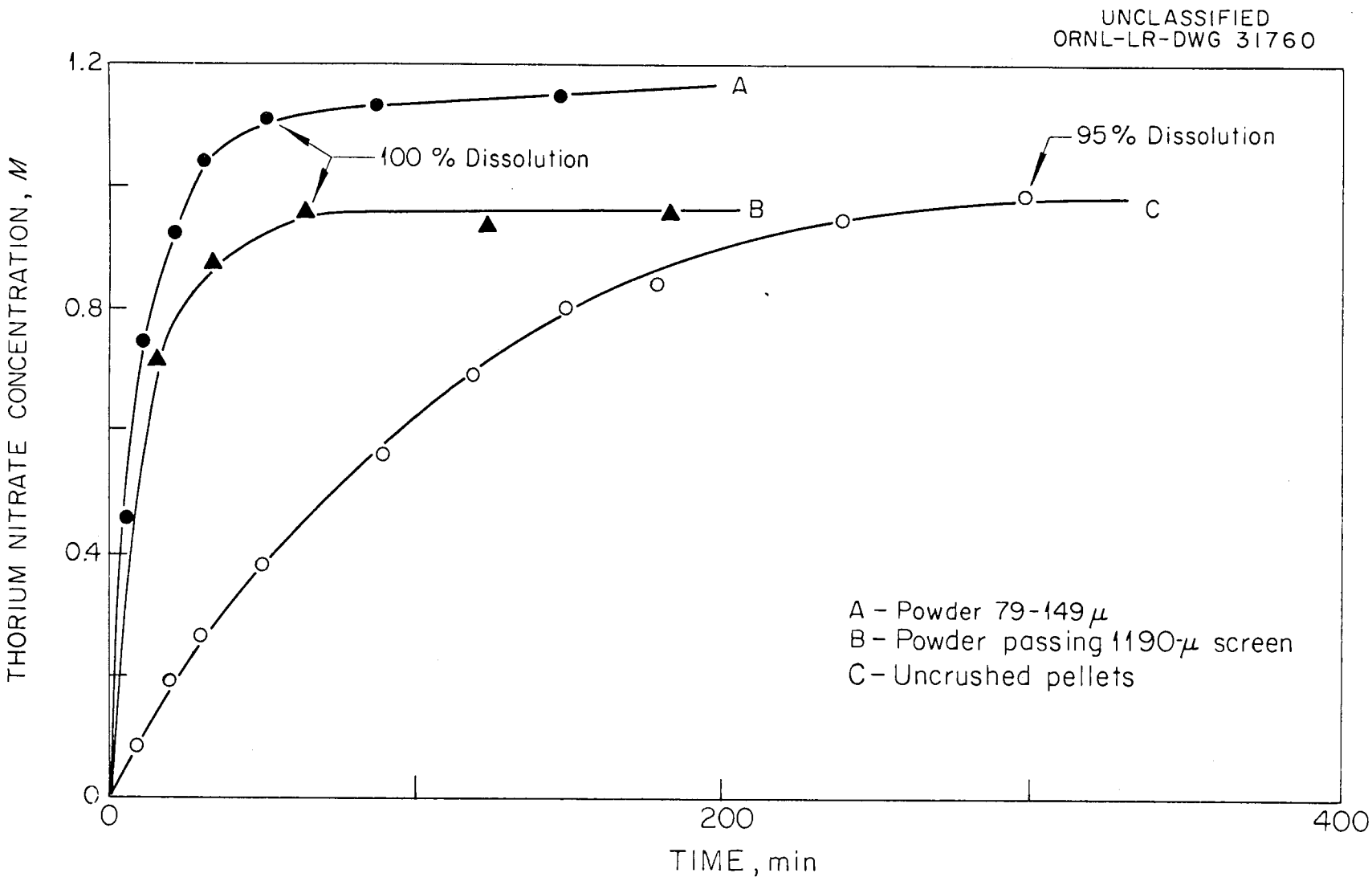

Fig. 5. Effect of pellet pulverization on time of dissolution of sintered 96% ThO_2–4% UO_2 pellets in boiling 13M HNO_3–0.04M NaF.

Table 3. Effect of Initial Volume/Surface Area Ratio on Dissolution Time in Boiling 13 M HNO_3--0.04 M NaF

Dissolvent volume: 100 ml
Specific surface area: ~1 cm^2/g
96% ThO_2--4% UO_2 sintered pellets

V/S, cm	Final $Th(NO_3)_4$ Conc, M	Dissolution Time, hr	Extent of Pellet Dissolution, %	Over-all Dissolution Rate,[a] mg/cm^2.min	Acid Consumed Per mole of ThO_2, moles
6.45	0.5	3.5	85	4.3	4.1
3.84	0.5	1.3	49	6.8	4.3
2.60	0.5	0.90	34	6.6	4.2
1.90	0.5	0.55	26	8.0	4.6
1.50	0.5	0.45	20	7.7	4.2
1.14	0.5	0.33	16	7.9	4.2
0.795	0.5	0.20	10	9.3	4.0
3.84	1.0	5.3	98	3.4	4.4
2.60	1.0	3.3	68	3.7	4.4
1.90	1.0	1.8	52	4.8	4.3
1.50	1.0	1.4	40	4.9	4.3
1.14	1.0	1.1	32	4.7	4.8
0.795	1.0	0.55	20	6.7	4.1
1.90	1.5	4.5	78	2.9	4.0
1.50	1.5	3.6	60	2.9	4.3
1.14	1.5	2.5	48	3.2	4.3
0.795	1.5	1.4	30	6.9	4.3
1.50	1.75	5.6	70	1.4	4.2
1.14	1.75	4.5	56	2.1	4.4
0.795	1.75	2.3	35	2.8	4.2

[a]Calculated from initial surface area; 0.041 M $UO_2(NO_3)_2$ is also produced when 1 M $Th(NO_3)_4$ is produced by the dissolutions.

Table 4. Dissolution Rates of 96% ThO_2-4% UO_2 Sintered Pellets in Various Dissolvents

Dissolvent	Temperature,[a] °C	Test Time, min	Rate,[b] mg/cm^2·min
4 M H_2SO_4	Boiling	2	0.034
6 M H_2SO_4		2	0.040
6 M H_2SO_4		180	0.026
6 M H_2SO_4-0.04 M NaF		180	0.041
3 M HNO_3		2	0.17
10 M HNO_3		2	0.14
13 M HNO_3		2	0.09
15.8 M HNO_3		2	0.20
2 M HF	90-95	2	0.60
5 M HF		2	0.23
9 M HF		2	0.24
12 M HF		2	0.18
2 M HCl-5 M HNO_3	Boiling	2	0.060
2 M HCl-5 M HNO_3		180	0.060
9 M HCl-4 M HNO_3		180	0.014
4 M HCl-12 M HNO_3		180	0.031
13 M HNO_3-0.04 M NaF	90-95	2	1.62
13 M HNO_3-0.04 M NaF		180	3.9
13 M HNO_3-0.04 M NaF	Boiling	180	5.7

[a]Tests at 90-95°C were done in polyethylene bottles immersed in a boiling water bath.

[b]Surface area changed with time so rates are comparable only for the same test time.

3.0 EXPERIMENTAL DETAILS

3.1 Materials and Chemicals

The pellets used for dissolution tests were fabricated by the American Lava Company. They are cylindrical in shape and were prepared by sintering at 1700°C. The composition is:

96.0 wt % thorium dioxide, ThO_2
0.4 wt % calcium fluoride, CaF_2 (as binder)
3.6 wt % uranium dioxide, UO_2

The pellets were 1/4-in. dia and 1/2 to 3/4 in. long.

Reagent grade chemicals were used in preparing all dissolvent solutions.

3.2 Apparatus

A cylindrical stainless steel vessel equipped with a pyrex glass bell connection to a reflux condenser was used for dissolutions in which nitric-fluoride mixtures were used. A parallel experiment in a Teflon vessel equipped with a polyethylene tubing condenser showed that the dissolution products resulting from mild attack of the stainless steel vessel by the dissolvent had no effect on the dissolution rate of the pellets. The volume of dissolvent used in all tests was 100 ml.

3.3 Dissolution Testing Procedures

Since the surface area of the cylindrical pellets changes as dissolution proceeds, two methods of dissolution testing were used: (1) determination of dissolution rates at very small and/or the same extent of pellet dissolution and (2) measurement of the increase in thorium concentration with time for different V/S ratios (initial dissolvent volume to surface area ratios). The surface area changes with dissolution because of the cylindrical shape of the pellets and because the initially smooth ceramic surface becomes roughened. Pitting of the pellets was observed in a few cases.

Dissolution rates were determined by measuring the quantity of material that reacts in a given time with the dissolvent. Preliminary tests showed that the dissolved thorium and uranium are in approximately

the same ratio as in the solid pellets. The rate was calculated, using the initial surface area as determined by measurement with calipers, from the relation

$$\text{Rate} = \frac{(\text{mg of material reacted})}{(\text{initial surface area})\ (\text{time})}$$

The buildup of thorium nitrate concentration in the dissolvent with time for the V/S ratios was determined by taking 1- to 2-ml samples of the solution at several preselected times during long-term dissolutions. The data obtained were used to calculate rates at different extents of pellet dissolution for the formation of thorium nitrate concentrations of interest. The thorium nitrate concentrations were corrected for the volume of solution removed for analysis. The inherent error in the procedure is 5-10%.

4.0 REFERENCES

1. F. W. Schuler, F. L. Steahly, R. W. Stoughton, "The Dissolution of Thorium Metal and Thorium Dioxide in HNO_3-HF and HNO_3-$(NH_4)_2SiF_6$ Mixtures," CC-3576 (June 30, 1945).

2. D. Peterson, R. Davis, "A Study of the Fluosilicate Catalyzed Reaction of Nitric Acid on Thorium Metal," ISC-266 (October, 1952).

3. A. H. Bushey, "Chemistry Unit Quarterly Progress Report," HW-31360 (May, 1954).

4. D. E. Ferguson, R. E. Leuze, W. E. Tomlin in "Homogeneous Reactor Quarterly Progress Report," p. 196, ORNL-1853 (January, 1955).

5. R. P. Wischow, "Examination of Irradiated ThO_2 Slugs for the U^{233}/Th Ratio," ORNL-CF-55-6-27 (June, 1955).

6. C. A. Goodall, J. L. Heptworth, R. L. Moore, R. A. Watts, Jr., "A Kinetic Study of the Fluoride Catalyzed Nitric Acid Dissolution of Thorium Metal," HW-40250 (November, 1955).

7. A. T. Gresky et al. Progress Reports: "Laboratory Development of the Thorex Process," ORNL-1367, 1431, 1518, and 1610 (November, 1951 to June, 1953).

8. A. T. Gresky, "The Thorex Process," Reactor Sci. Technol., 4 (2): 43-57, TID-2013 (June, 1954).

9. D. L. Foster, J. E. Savolainen, R. G. Wymer, "Nuclear Reactor Fuel Dissolutions," Paper 547, International Conference on the Peaceful Uses of Atomic Energy, Geneva, August, 1955 (Original, ORNL-CF-55-9-102).

10. R. E. Blanco, "Dissolution and Feed Adjustment," Symposium on the Reprocessing of Irradiated Fuels, Book 1, pp. 22-44, TID-7534 (May, 1957).

11. E. O. Nurmi, D. L. Foster, "Thorium Dissolution Studies for Aqueous Fuel Reprocessing," Paper presented at 3rd annual meeting of American Nuclear Society, Pittsburgh (June 10-12, 1957).

12. N. W. Dodgen, G. K. Rollefson, "The Complex Ions Formed by Iron and Thorium with Fluoride in Acid Solution," J. Am. Chem. Soc., 71: 2600-7 (1949).

13. P. A. Day, R. W. Stoughton, "The Chemistry of Thorium in Aqueous Solution. I. Some Organic and Inorganic Complexes," J. Am. Chem. Soc., 72: 5662-7 (1950).

5.0 APPENDIX

Since the true surface area of the pellets was not determined and the adsorption phenomena occurring on the surface were not investigated, it was not possible to give the data a fundamental kinetic interpretation. However, for practical purposes an apparent order of reaction with respect to nitric acid was calculated from the data in Table 3. Such a calculation permits, within limits, assigning of a numerical order-of-magnitude effect of nitric acid concentration on the dissolution rate. It should be clearly emphasized that this apparent order is not proposed to be the true kinetic order of the reaction. The calculation is justified entirely on the basis of its usefulness.

By assuming the general equation for the reaction between a dissolved substance and the surface of an insoluble solid and that, for the purpose of this calculation, the two components UO_2 and ThO_2 need not be considered separately, the equation

$$\frac{\Delta W}{\Delta t} = k \left[A \right] \left[HNO_3 \right]^n \qquad (1)$$

was derived where

$\frac{\Delta W}{\Delta t}$ = loss of pellet weight with time

k = the specific rate constant

A = surface area of the pellet

$\left[HNO_3 \right]$ = nitric acid concentration

n = apparent order of reaction with respect to nitric acid

By defining R as $\frac{\Delta W}{\Delta t}/A$ and rearranging Eq. 1, the following equation results:

$$R = k \left[HNO_3 \right]^n \qquad (2)$$

If log R is then plotted against log $\left[HNO_3\right]$, a straight line of slope n should result when the order of reaction does not change with nitric acid concentration and with thorium nitrate concentration. Figure 6 is a plot of log R versus nitric acid concentration for solutions containing 0, 0.3, and 0.8 M $Th(NO_3)_4$. The apparent order changes with both nitric acid and thorium nitrate concentration, but the curves are approximately linear in the region 2-8 M HNO_3, after which the slope rapidly decreases with increasing nitric acid concentration. In the 2-8 M HNO_3, the apparent order is approximately 3 for solutions containing 0 M $Th(NO_3)_4$ and approximately 4 for solutions containing 0.3 and 0.8 M $Th(NO_3)_4$. From 8 to 13 M HNO_3, all curves show about first order dependence.

The practical implications of the results are evident. Apparently, little is gained by attempting to dissolve the pellets in 13 M HNO_3--0.04 M NaF solutions to much greater than 1 M $Th(NO_3)_4$, at which concentration the nitric acid would be reduced to less than 8 M.

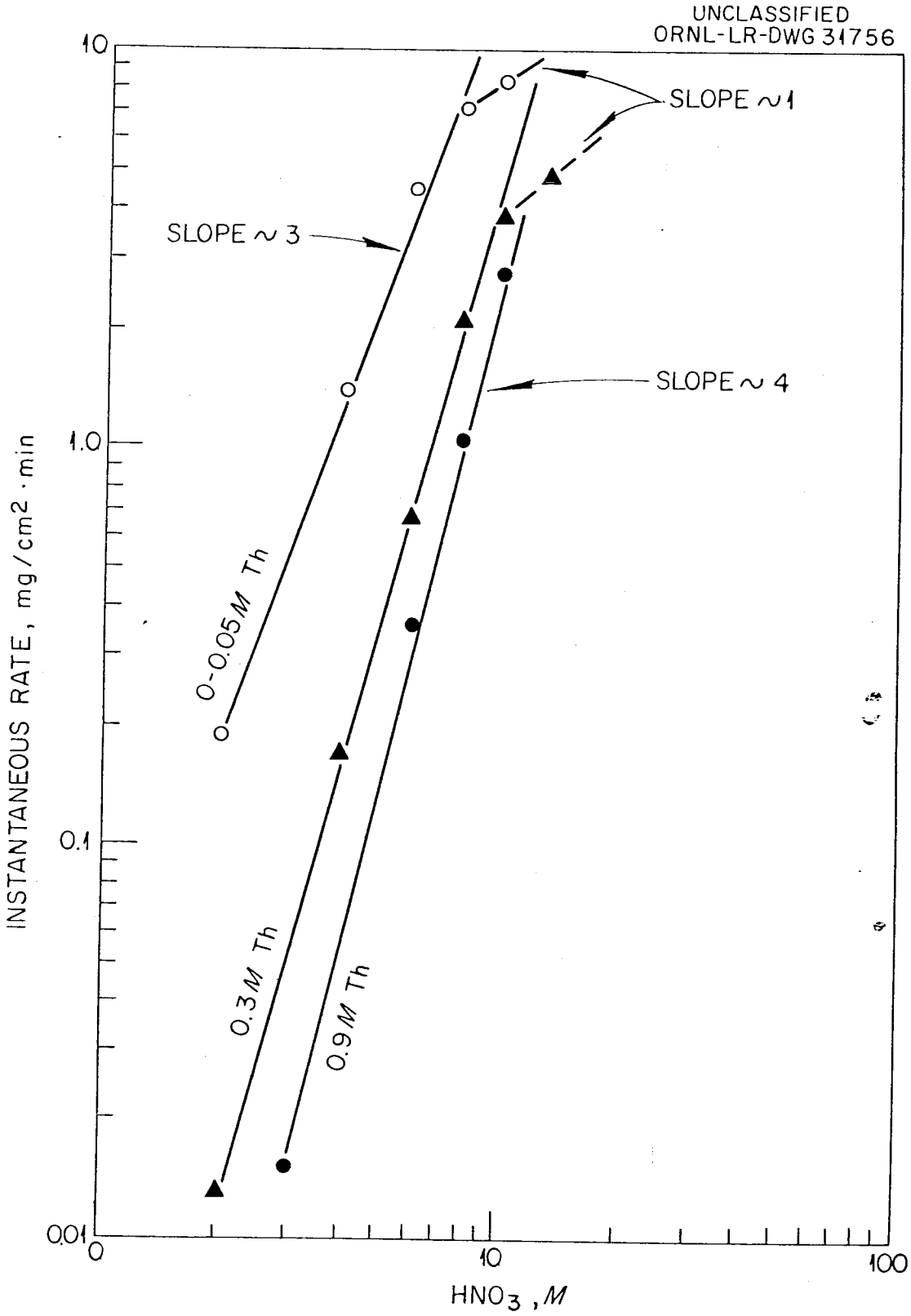

Fig. 6. Apparent order of reaction of 96% ThO_2–4% UO_2 pellets with respect to acid concentration.

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R.C.
28. A. M. Weinberg
29. L. B. Emlet (K-25)
30. J. P. Murray (Y-12)
31. J. A. Swartout
32. E. H. Taylor
33. E. D. Shipley
34-35. F. L. Culler
36. M. L. Nelson
37. W. H. Jordan
38. C. P. Keim
39. J. H. Frye, Jr.
40. S. C. Lind
41. A. H. Snell
42. A. Hollaender
43. K. Z. Morgan
44. M. T. Kelley
45. T. A. Lincoln
46. R. S. Livingston
47. A. S. Householder
48. C. S. Harrill
49. C. E. Winters
50. H. E. Seagren
51. D. Phillips
52. W. K. Eister
53. F. R. Bruce
54. D. E. Ferguson
55. R. B. Lindauer
56. H. E. Goeller
57. C. W. Hancher
58. R. A. Charpie
59. J. A. Lane
60. M. J. Skinner
61. R. E. Blanco
62. G. E. Boyd
63. W. E. Unger
64. R. R. Dickison
65. A. T. Gresky
66. E. D. Arnold
67. C. E. Guthrie
68. J. W. Ullmann
69. K. B. Brown
70. K. O. Johnsson
71. J. C. Bresee
72. W. D. Bond
73. G. I. Cathers
74. W. E. Clark
75. W. Davis
76. O. C. Dean
77. L. M. Ferris
78. J. R. Flanary
79. A. H. Kibbey
80. F. G. Kitts
81. R. E. Leuze
82. J. P. McBride
83. R. A. McNees
84. E. L. Nicholson
85. J. J. Perona
86. R. H. Rainey
87. J. T. Roberts
88. J. E. Savolainen
89. C. D. Watson
90. W. H. Lewis
91. R. C. Waugh
92. J. I. Federer
93. D. L. Katz (consultant)
94. G. T. Seaborg (consultant)
95. M. Benedict (consultant)
96. C. E. Larson (consultant)
97. L. Squires (consultant)
98. J. H. Rushton (consultant)
99. ORNL - Y-12 Technical Library, Document Reference Section

EXTERNAL DISTRIBUTION

100. Division of Research and Development, AEC, ORO
101-102. AEC, Washington (1 copy ea. to F. P. Baranowski and F. Kerze)
103-104. Hanford Operations Office (1 copy ea. to L. P. Bupp and O. F. Hill)
105-106. Brookhaven National Laboratory (1 copy ea. to L. P. Hatch and B. Manowitz)
107. Argonne National Laboratory (S. Lawroski)
108. duPont, Savannah River (J. W. Morris)
109. Atomics International (E. E. Motta)
110. Idaho Chemical Processing Plant (C. E. Stevenson)
111. duPont, Wilmington (V. R. Thayer)
112. Babcock & Wilcox (L. Weissert)
113-629. Given distribution as shown in TID-4500 (14th ed.) under Chemistry-Separation Processes for Plutonium and Uranium (75 copies - OTS)