ORNL
MASTER COPY

43

ORNL-3695
UC-4 – Chemistry
TID-4500 (37th ed.)

DISSOLUTION OF HIGH-DENSITY UO_2, PuO_2, AND UO_2-PuO_2 PELLETS IN INORGANIC ACIDS

Armando L. Uriarte
Robert H. Rainey

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

Printed in USA. Price $3.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Department of Commerce, Springfield, Virginia

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-3695

Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

DISSOLUTION OF HIGH-DENSITY UO_2, PuO_2, AND UO_2-PuO_2 PELLETS IN INORGANIC ACIDS

Armando L. Uriarte* Robert H. Rainey

APRIL 1965

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated By
UNION CARBIDE CORPORATION
For The
U.S. ATOMIC ENERGY COMMISSION

*Junta de Energia Nuclear, Madrid, Spain.

CONTENTS

Page

Abstract 1

1. Introduction 2

2. Experimental Procedure 3

3. Instantaneous Dissolution Rates 6

3.1 Dissolution Rates of Sintered UO_2 Pellets 6

3.1.1 In Nitric Acid 7
3.1.2 In HNO_3-HF 7
3.1.3 In HNO_3-HF-$Al(NO_3)_3$ 13
3.1.4 In HNO_3--0.3 M $Al(NO_3)_3$ 13
3.1.5 In HNO_3 Containing $NaNO_3$ or $LiNO_3$ or $Al(NO_3)_3$ 13
3.1.6 In HNO_3 Containing $UO_2(NO_3)_2$ 15
3.1.7 In HNO_3 Containing $NaNO_2$ 15
3.1.8 Of Varying Density 15

3.2 Dissolution Rates of Sintered PuO_2 Pellets 22

3.2.1 In HNO_3 22
3.2.2 In HNO_3-HF 22
3.2.3 In HNO_3-HF-$Al(NO_3)_3$ 25
3.2.4 In HNO_3-Ce(IV) 25
3.2.5 In HNO_3-O_3 30
3.2.6 In HNO_3-H_2O_2 30
3.2.7 In HNO_3-$Na_2Cr_2O_7$ 30
3.2.8 In HNO_3 Containing $NaNO_3$ or $LiNO_3$ 30
3.2.9 In HNO_3-HCl 30
3.2.10 Of Varying Density 31

3.3 Dissolution Rates of Sintered PuO_2-UO_2 Pellets 31

3.3.1 Of Varying PuO_2 Concentration 31
3.3.2 In HNO_3 33

4. Time Required to Dissolve Pellets Completely 36

4.1 Theoretical Dissolution Time 36

4.1.1 Of Smooth Pellets 36
4.1.2 Roughening-Factor Calculations 36

4.2 Total Dissolution of UO_2 Pellets 38

4.2.1 Effect of Excess Acid 38
4.2.2 Variation in Surface Area 38
4.2.3 Variation with Source of Pellets 39

4.3 Total Dissolution of PuO_2 Pellets 39

CONTENTS
(Continued)

Page

4.4 Total Dissolution of PuO_2-UO_2 Pellets 45
4.4.1 Effect of Fabrication Procedure 45
4.4.2 Preparation of Purex-Type Solvent Extraction Feed Solutions 45
4.4.3 Experiments Using Cyclic Operations 49
4.4.4 Dissolution of Irradiated Pellets 51
4.4.5 Recommendations for a Commercial Facility 53

5. References 54

6. Appendix 55
6.1 Tables of Data 55
6.2 FORTRAN Codes for Calculating Dimensions During Dissolution . 76

DISSOLUTION OF HIGH DENSITY UO_2, PuO_2, AND UO_2-PuO_2 PELLETS IN INORGANIC ACIDS

Armando L. Uriarte Robert H. Rainey

ABSTRACT

A laboratory study was made of the initial instantaneous dissolution rates (IDR) and total dissolution times of unirradiated, commercially prepared UO_2, PuO_2, and PuO_2-UO_2 pellets in boiling nitric acid alone and with additives. The UO_2 dissolved readily in nitric acid alone; PuO_2 dissolved slowly even with the addition of fluoride. Pellets containing as much as 28% PuO_2 in UO_2 dissolved in nitric acid alone when fabrication procedures indicated that solid solutions were formed, but part of the plutonium remained undissolved from pellets which were probably not solid solutions. Since the present state of the art of pellet fabrication does not ensure that the plutonium will be in solid solution in all pellets, and since complete dissolution of plutonium is required in commercial fuel processing, the use of fluoride for the dissolution of PuO_2-UO_2 pellets is indicated.

Empirical equations for approximating the dissolution rates are as follows:

$$IDR_{UO_2} = 480\ (\underline{M}\ HNO_3)^2\ e^{-0.091\ (\%\ TD)},$$

$$IDR_{PuO_2} = 5 \times 10^3 (\underline{M}\ HNO_3)^4\ e^{-0.27\ (\%\ TD)},$$
$$+ 4 \times 10^7 (\underline{M}\ HNO_3)^4 (\underline{M}\ HF)^{1.4}\ e^{-0.27\ (\%\ TD)},$$

$$IDR_{PuO_2\text{-}UO_2} = (IDR_{PuO_2})^n\ (IDR_{UO_2})^{1-n},$$

where (% TD) is the percent of theoretical density of the pellet, ($\underline{M}$ HNO_3) and ($\underline{M}$ HF) are the molar concentration of the acids, and (n) is the mole fraction of PuO_2 in the UO_2-PuO_2 solid solution.

Due to roughening of the pellets while dissolving, the time to dissolve 95% was only about a third the time that would be calculated from these rates.

It was concluded that PuO_2-UO_2 pellets presently considered for power reactors can be dissolved in a reasonable time. For example, 28% PuO_2--72% UO_2 solid solution pellets (0.17 cm x 0.55 cm diameter) with densities that were 93% of theoretical dissolved in less than 6 hr in 6 $\underline{M}$ HNO_3 to produce a solution 0.57 $\underline{M}$ in plutonium, 1.25 $\underline{M}$ in uranium, and 3 $\underline{M}$ in HNO_3.

1. INTRODUCTION

An important class of nuclear power reactor fuels consists of UO_2, PuO_2-UO_2, or ThO_2-UO_2 pellets or compacts clad with stainless steel or Zircaloy-2. After irradiation, the fuel elements are processed to recover the unburned fissile materials for recycle to the reactors. Processing will consist either in the chemical removal of the cladding material, such as by dissolving the stainless steel cladding in sulfuric acid[1] or Zircaloy-2 in ammonium fluoride or by shearing the elements into small pieces.[2] The exposed oxides can then be dissolved in nitric acid and the fissile and fertile materials recovered and separated from fission products and other impurities by solvent extraction.

Previous workers have reported the effect of temperature, stirring rate, etc., on the dissolution rate of UO_2 pellets on laboratory-scale[3] and on a semiengineering scale.[4] Limited studies with PuO_2[5] and UO_2-PuO_2[6] have been reported, but no systematic investigations were found in the literature. Laboratory studies on dissolving ThO_2 have also been reported.[7]

This report presents a systematic study of the dissolution of PuO_2-UO_2 pellets as a function of dissolvent composition, pellet composition, and pellet fabrication procedure. First, the initial instantaneous dissolution rates of UO_2, PuO_2, and various PuO_2-UO_2 mixtures were determined in boiling nitric acid, with and without additives. Next, the variation in the surface area of the pellets was determined to obtain the effective area to be used in calculating the time for complete dissolution. Finally, the time for complete dissolution was measured and compared with that calculated from the instantaneous dissolution rate and surface area.

The data in this report were obtained from single pellets except for a few feed-preparation experiments. None of the pellets had been irradiated, but the fuel from reactors will have been irradiated to as much as 100,000 Mwd/metric ton. The centers of some irradiated pellets are expected to reach the fusion temperature, and many of them will have been broken from thermal shock. Therefore, the dissolution of our intact unirradiated pellets may be different from that of irradiated reactor fuel. A continuation

of our program will include a comparison of the dissolution characteristics of highly irradiated pellets with the rates for unirradiated pellets given in this report.

The assistance of the following people at ORNL is gratefully acknowledged. R. C. Lovelace gave valuable assistance in the experimental program. Analyses were made by members of the Analytical Chemistry Division under the supervision of W. R. Laing, C. E. Lamb, and J. H. Cooper. Photomicrographs were prepared by members of the Metals and Ceramics Division under the supervision of R. J. Gray. Members of the Mathematics Division helped in formulation of equations and the use of computers. Samples of pellets were obtained from many sources, but we are particularly grateful to C. S. Caldwell, of Nuclear Materials and Equipment Company for his assistance in providing PuO_2 and PuO_2-UO_2 pellets of known history.

Many detailed tables of data are included in Appendix I. The FORTRAN codes used in calculating the radius and surface area of pellets are included as Appendix II.

2. EXPERIMENTAL PROCEDURE

Pellets used in this study were obtained from commercial sources when available. Except when so designated, the UO_2 pellets were prepared by W. R. Grace and Company, Davison Chemical Division, Erwin, Tennessee. These pellets were 1.06 cm in diameter and 1.59 cm long; they had a density of 10.3 ± 0.1 g/cm^3, which corresponds to 93.8% of the theoretical density. These Davison I pellets were different from Davison II pellets in that they were glossier and had a lower initial dissolution rate. The pellets were washed with acetone to remove traces of grease, and then they were air dried. They were then weighed to ±1 mg; the length and diameter were measured ±0.001 in.; and the apparent surface area and bulk density were calculated from these values for use in rate calculations. The actual surface areas of single pellets could not be determined. In the instantaneous dissolution rate experiments, less than 3% of the pellet was dissolved and therefore the change in surface area during the experiment was not

considered. Under these conditions, the difference in rate between duplicate pellets was small. A separate pellet was used for each experiment.

The PuO_2 and PuO_2-UO_2 pellets were prepared by Nuclear Materials and Equipment Corporation, Apollo Pennsylvania.[8] These pellets were 0.69 cm in diameter and 0.55 cm long. Except when the effect of density was being studied, pellets were chosen which had densities of 10.3 ± 0.1 g/cm^3, about 90% of the theoretical density. These pellets were weighed to ±1 mg and the lengths and diameters were measured to ±0.001 cm. To avoid the hazard of fire in the glove boxes, the pellets were not washed with acetone before dissolving, as were the UO_2 pellets. Only three PuO_2 pellets were used in the dissolution rate experiments. Solutions were analyzed by alpha counting. Rate calculations by weight loss were impractical because only about 0.05% of the pellet was dissolved in each test.

In our study of the dissolution of PuO_2-UO_2 pellets, we were limited by the lack of an analytical method for determining whether the PuO_2 was in solid solution with the UO_2. It seems that the dissolution itself is one of the most accurate and sensitive methods for this determination; therefore, we assumed that a uniform, proportional dissolution of the plutonium and uranium in nitric acid without fluoride indicates a solid solution. We recognize that the homogeneity of the solid solution must also affect the rate, but we were unable to study methods for compensating for this parameter due to the limited variety of pellets available.

The PuO_2-UO_2 pellets were fabricated by two methods. In one method, previously prepared UO_2 and PuO_2 were mechanically blended before being pressed into a "green" pellet. In the other method, $Pu(OH)_4$ and $(NH_4)_2U_2O_4$ were coprecipitated and then fired in a reducing atmosphere to the dioxides, which were then pressed into pellets. In either case, the green pellets were sintered in a reducing atmosphere to the desired final density.[8] The dissolution of the two types of pellets was different. Apparently the finer, more intimately mixed crystals formed by the coprecipitation method will form solid solution at a lower temperature or shorter time than do the mechanically blended oxides. With either type of pellet, sintering for a long time at high temperatures resulted in pellets in which the

PuO_2 was apparently in solid solution. As the concentration of PuO_2 increases, the time and/or temperature required for solid solution formation also increases.

The dissolver vessels were three-neck glass flasks, each equipped with a glass reflux condenser, a thermometer, and a port for inserting the pellet and removing samples. A platinum liner was inserted into the condenser when the solution contained fluoride.

The pellet was placed in a basket made of stainless steel for most tests, but of platinum when the dissolver solution contained fluoride. The acid was preheated to the boiling temperature, and then the basket and pellet were immersed in the solution. After a measured time, the basket was removed, the pellet washed with water and acetone, and then air dried. The pellet was then reweighed, measured, and the solution analyzed. In early experiments with UO_2, the instantaneous dissolution rate was calculated from both the loss of weight and the analysis of the solution. The physical measurement was discontinued when the two methods were shown to give the same results.

The variation in the rate (milligrams dissolved per unit of time) was measured as the pellet dissolved completely by sampling the solution periodically. Acid of the same composition as the original dissolver solution was added to the vessel to replace the sample removed. Since these experiments were made with a large excess of acid, there was little variation in acidity during the experiment; however, a few duplicate experiments were made without intermediate sampling in order to determine more accurately the time for complete dissolution.

No corrections were made for the differences in dissolution rate caused by differences in the boiling temperatures of the various solutions.

When data could be plotted so as to result in an apparent straight line, least-squares methods were used to determine the line of best fit.

3. INSTANTANEOUS DISSOLUTION RATES

The instantaneous dissolution rates of the pellets were determined to elucidate the dissolution chemistry and to obtain empirical mathematical equations for calculating process variables. The variables investigated included nitric acid concentration, total nitrate concentration, the addition of oxidizing agents and fluoride to nitric acid, as well as the effect of the density, composition, and method of fabrication of the pellets.

3.1 Dissolution Rates of Sintered UO_2 Pellets

Since the conditions for dissolving urania have been published,[3] our study was primarily to confirm previous conclusions using commercial UO_2 pellets and to develop techniques applicable to PuO_2 and PuO_2-UO_2 pellets. According to the literature, UO_2 dissolves in nitric acid as follows:

$$UO_2 + 4HNO_3 \longrightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O \text{ (refs 6,9)} \qquad (1)$$

$$UO_2 + 8/3HNO_3 \longrightarrow UO_2(NO_3)_2 + 2/3NO + 4/3H_2 \text{ (ref 6)} \qquad (2)$$

$$UO_2 + 3HNO_3 \longrightarrow UO_2(NO_3)_2 + 1/2NO + 1/2NO_2 + 3/2H_2O \text{ (ref 1)} . \qquad (3)$$

In the presence of oxygen, the following reaction takes place:

$$UO_2 + 1/2O_2 + 2HNO_3 \longrightarrow UO_2(NO_3)_2 + H_2O \text{ (ref 9)} . \qquad (4)$$

Our study showed that although the rate is proportional to the second power of the nitric acid concentration, the amount of acid consumed varies with acidity. As has been observed with uranium metal,[10] there is therefore no general chemical equation to represent the reactions. However, if the HNO_3 concentration is less than 8 N, and if air is excluded, the following reaction seems to be most applicable:

$$UO_2 + 4HNO_3 \longrightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O . \qquad (1)$$

3.1.1 In Nitric Acid

The instantaneous dissolution rate (IDR) of UO_2 pellets increased from 0.9 to 60 mg cm^{-2} min^{-1} as the concentration of the nitric acid increased from 2 to 15.6 M (Table A-1,* Fig. 1). Three experiments were made at each nitric acid concentration. The logarithmic plots of the rate vs nitric acid concentration are linear, and, the equation, calculated by a least-squares method, is: $IDR = 0.207\ (N\ HNO_3)^{2.12}$ from physical measurements, and $IDR = 0.215\ (N\ HNO_3)^{2.03}$ from chemical analysis, where IDR is in mg UO_2 cm^{-2} min^{-1}. Since the results from chemical analysis and physical measurements are so nearly identical, physical measurements will be omitted from figures in the remainder of this report.

These data agree within experimental error with those from previous experiments by others at ORNL[4] over the range of their experiments. We found, however, that the semi-logarithmic relation they reported cannot be extrapolated to give the rates we obtained in high concentrations of nitric acid (Fig. 2).

3.1.2 In HNO_3-HF

The dissolution rate of UO_2 pellets decreases with increasing hydrofluoric acid concentration when the HNO_3 concentration is greater than 6 M HNO_3, but increases with HF concentration when the HNO_3 concentration is less than 6 M (Table A-2). The logarithmic plots of rate vs hydrofluoric acid concentration at constant nitric acid concentrations are linear when the HF concentration is greater than 0.005 M (Fig. 3) and are described by the equation in Table 1.

The variation in dependence of the dissolution rate on the HNO_3 concentration decreased from about second power at 0.005 to 0.01 M HF to about first power at 0.1 M HF (Table 2, Fig. 4).

A film of UF_4 formed on the pellets during the dissolution with HNO_3-HF solutions and gave the pellets a green color.

---

*All tables whose numbers are prefixed by the letter A are found in the Appendix.

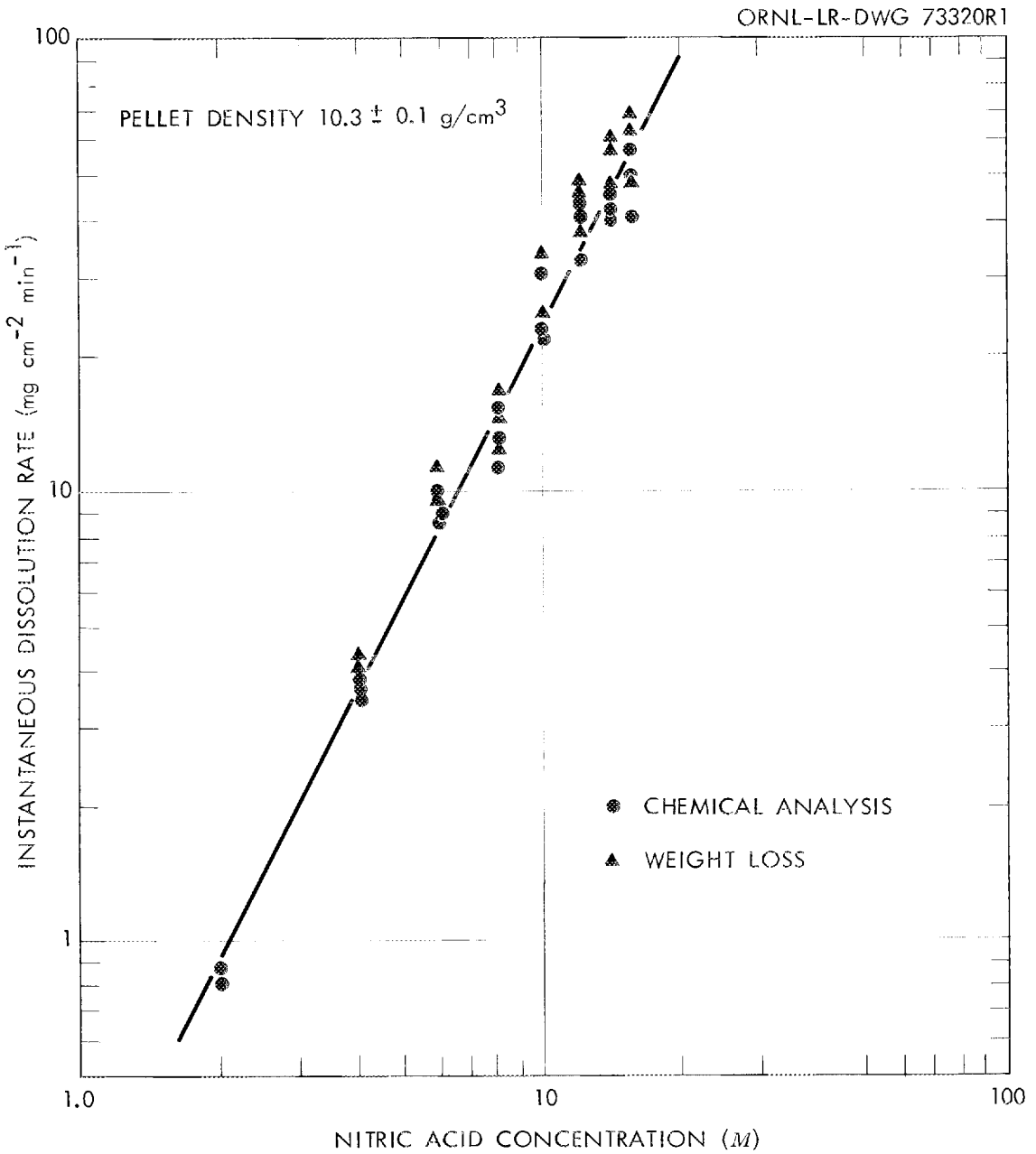


Fig. 1. Effect of Concentration on the Rate of Dissolution of UO_2 Pellets in Boiling Nitric Acid Solutions.

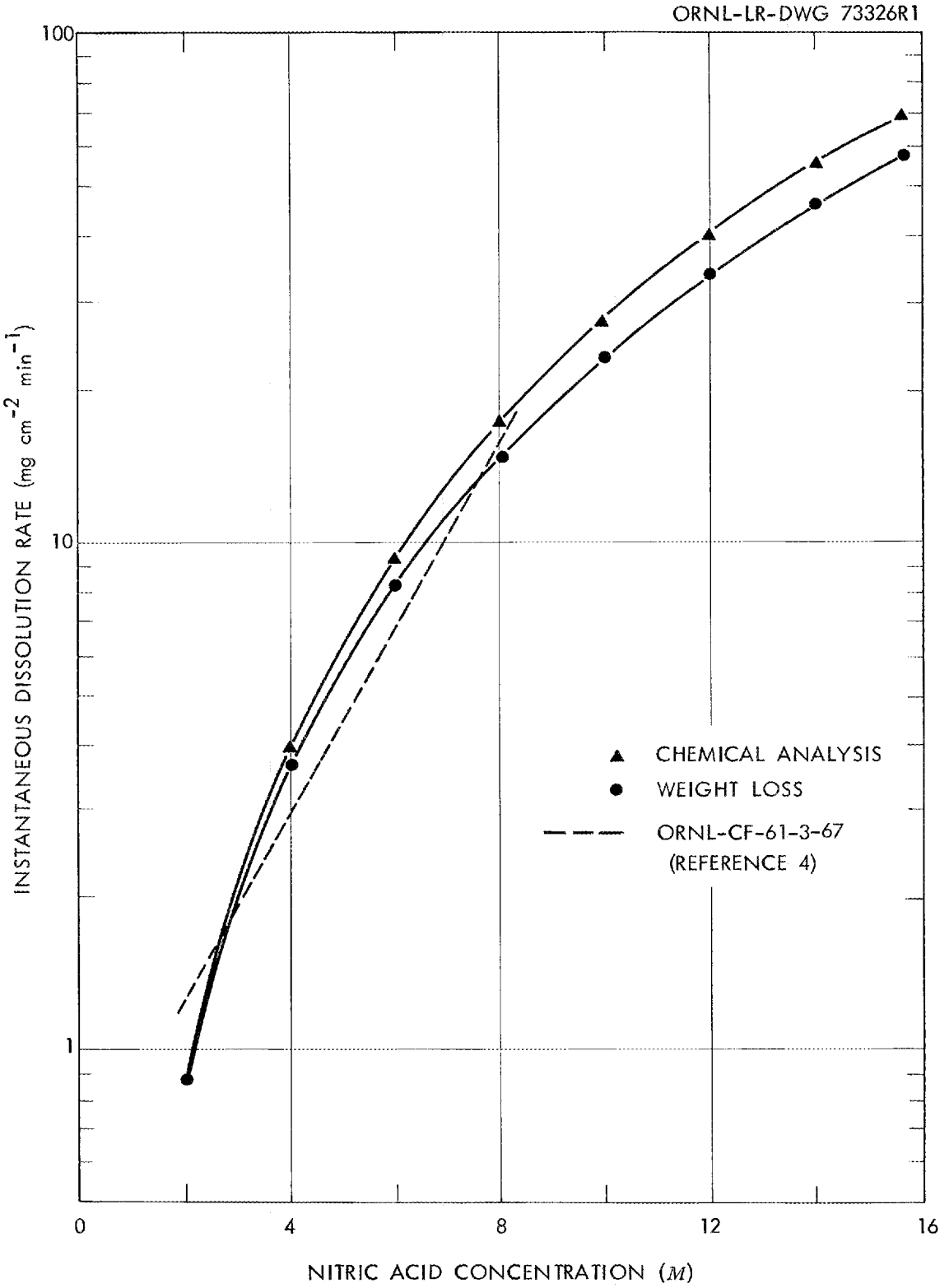


Fig. 2. Comparison of Present and Previous ORNL Data on the Rates of Dissolution of UO_2 Pellets in Nitric Acid.

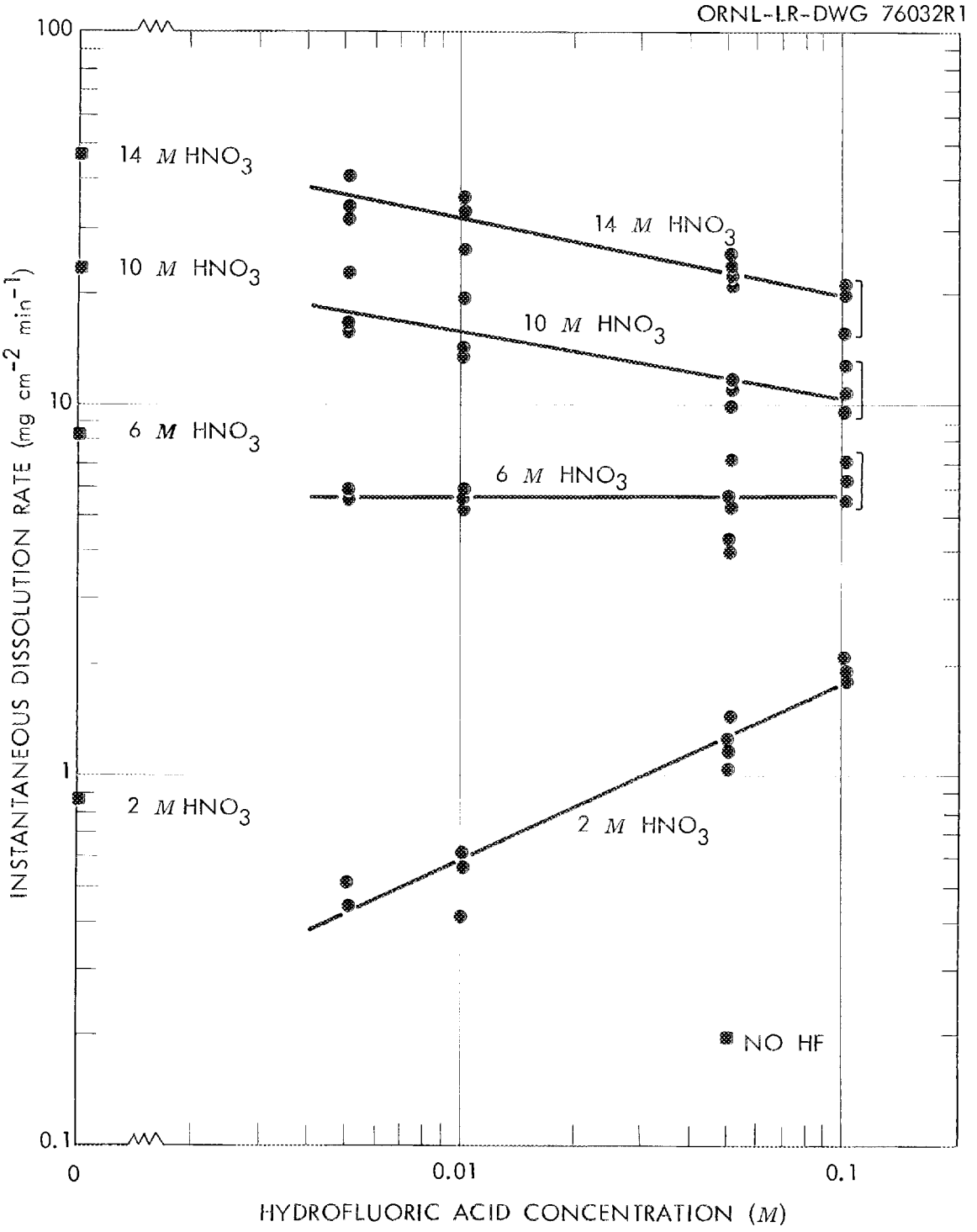


Fig. 3. Dissolution Rates of UO_2 Pellets in Nitric-Hydrofluoric Acid: Effect of Hydrofluoric Acid Concentration.

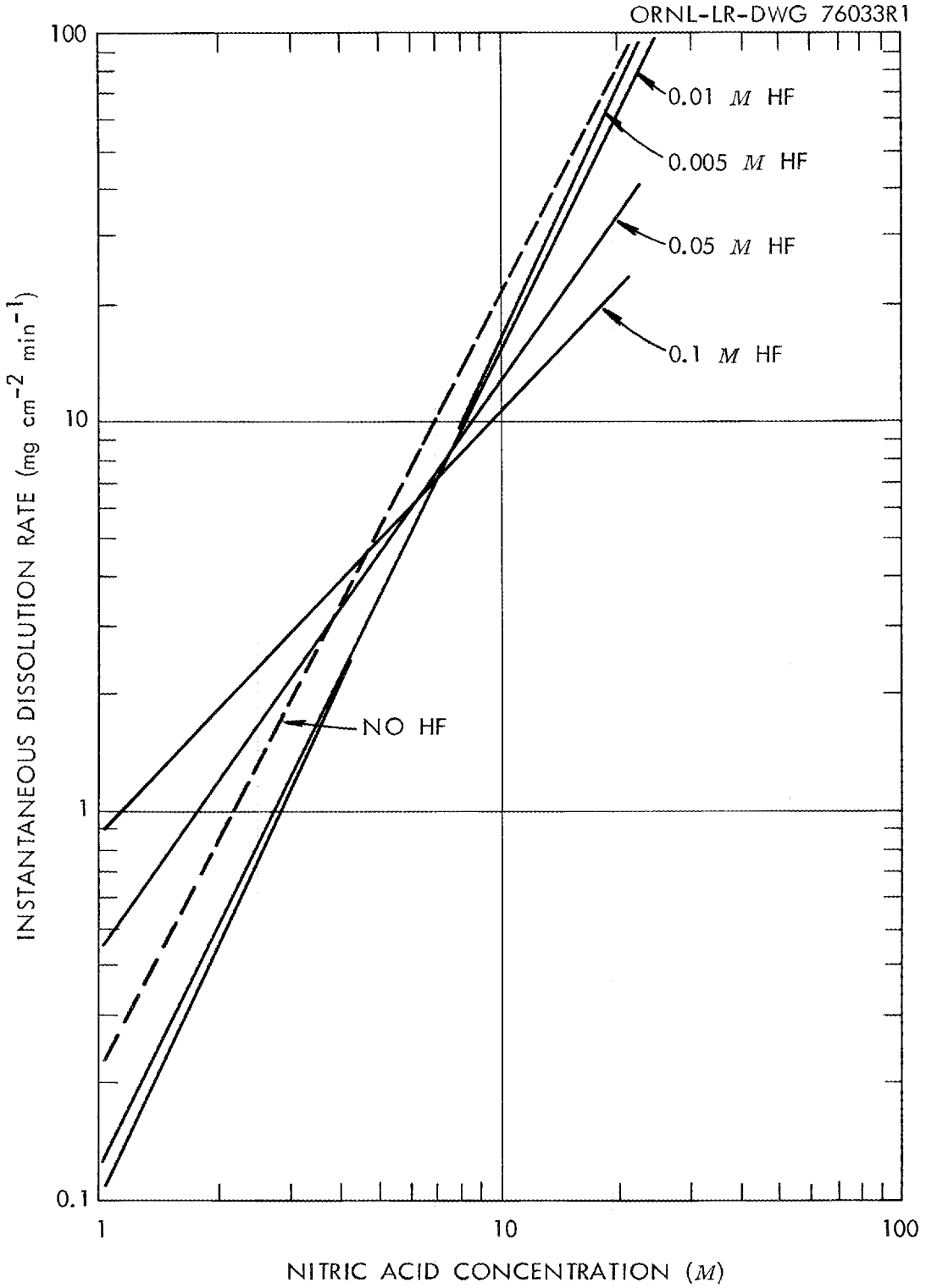


Fig. 4. Effect of Nitric Acid Concentration on Dissolution Rates of UO_2 Pellets in Nitric Hydrofluoric Acid.

Table 1. Dissolution Rates of UO_2 Pellets in HNO_3-HF Solutions: Effect of HF Concentration

Pellet Density: 10.3 ± 0.1 g/cm^3

Acid Concentration (M)		Parameters of Equation: log R = A log (M HF) - C, R = Inst. Diss. Rate				Range of Inst. Diss. Rate (mg cm^{-2} min^{-1})	
		Physical Analysis		Chemical Analysis			
HNO_3	HF	A	C	A	C	Physical	Chemical
2	0.005-0.1	0.4646	0.7098	0.4784	0.7264	0.44- 1.8	0.42-1.8
6	0.005-0.1	-0.0210	0.7215	0.0033	0.7546	5.80- 5.60	5.6 -5.8
10	0.005-0.1	-0.1686	0.8976	-0.1792	0.8417	19.50-11.50	18 - 10
14	0.005-0.1	-0.2039	1.1513	-0.2057	1.9025	42-22	37 - 20

Table 2. Dissolution Rates of UO_2 Pellets in HNO_3-HF Solutions: Effect of HNO_3 Concentration

Pellet Density: 10.3 ± 0.1 g/cm^3

Acid Concentration (M)		Parameters of Equation: log R = A log (M HNO_3) - C, R = Inst. Diss. Rate				Range of Inst. Diss. Rate (mg cm^{-2} min^{-1})	
		Physical Analysis		Chemical Analysis			
HNO_3	HF	A	C	A	C	Physical	Chemical
2-14	0.1	1.1217	-0.0580	1.0896	-0.0447	1.90-18	1.90-16
2-14	0.05	1.5455	-0.4017	1.4781	-0.3639	1.15-24	1.20-22
2-14	0.01	2.1482	-0.9003	2.1102	-0.9040	0.58-37	0.53-33
2-14	0.005	2.2976	-0.9868	2.2462	-0.9992	0.50-43	0.48-38

3.1.3 In HNO_3-HF-$Al(NO_3)_3$

The addition of aluminum nitrate (Al/F mole ratio of 3) to the nitric acid-hydrofluoric acid system to decrease the corrosion of stainless steel equipment is a common practice in reactor fuel processing. The addition of aluminum negates the effect of the fluoride on the dissolution of the UO_2 pellets (Table A-3, Fig. 5). The rates are slightly higher than with nitric acid alone (see Sec 4.1.4) and the dissolution rate remains proportional to the square of the acid concentration (Table 3).

Table 3. Dissolution Rates of UO_2 Pellets in HNO_3-HF-$Al(NO_3)_3$ Solutions: Effect of HNO_3 Concentration

Pellet Density: 10.3 ± 0.1 g/cm^3
Al/F mole ratio = 3

Concentrations (M)			Parameters of Equations: log R = A log (N HNO_3) - C, Physical Analysis		Chemical Analysis	
HNO_3	HF	$Al(NO_3)_3$	A	C	A	C
2-14	0.005	0.015	2.1141	-0.6693	2.0605	-0.6639
2-14	0.01	0.03	1.9780	-0.5190	1.9329	-0.5259
2-14	0.05	0.15	2.0195	-0.5371	1.9674	-0.5163
2-14	0.1	0.3	1.8865	-0.3590	1.8575	-0.3556

3.1.4 In HNO_3--0.3 M $Al(NO_3)_3$

The dissolution rate of UO_2 in nitric acid that is 0.3 M in aluminum nitrate is the same as with HNO_3--0.1 M HF--0.3 M aluminum nitrate (Table A-4). This indicates that the slight increase in rate for UO_2 with boiling mixtures of HNO_3-HF-$Al(NO_3)_3$ (Al/F mole ratio 3) is due to the presence of the aluminum nitrate and that fluoride has no effect.

3.1.5 In HNO_3 Containing $NaNO_3$, $LiNO_3$, or $Al(NO_3)_3$

Experiments with boiling 2 to 13 M HNO_3 containing 0 to 8 M $NaNO_3$, $LiNO_3$, or $Al(NO_3)_3$ showed that the dissolution rate is proportional to the second power of the total nitrate concentration. The salt in these

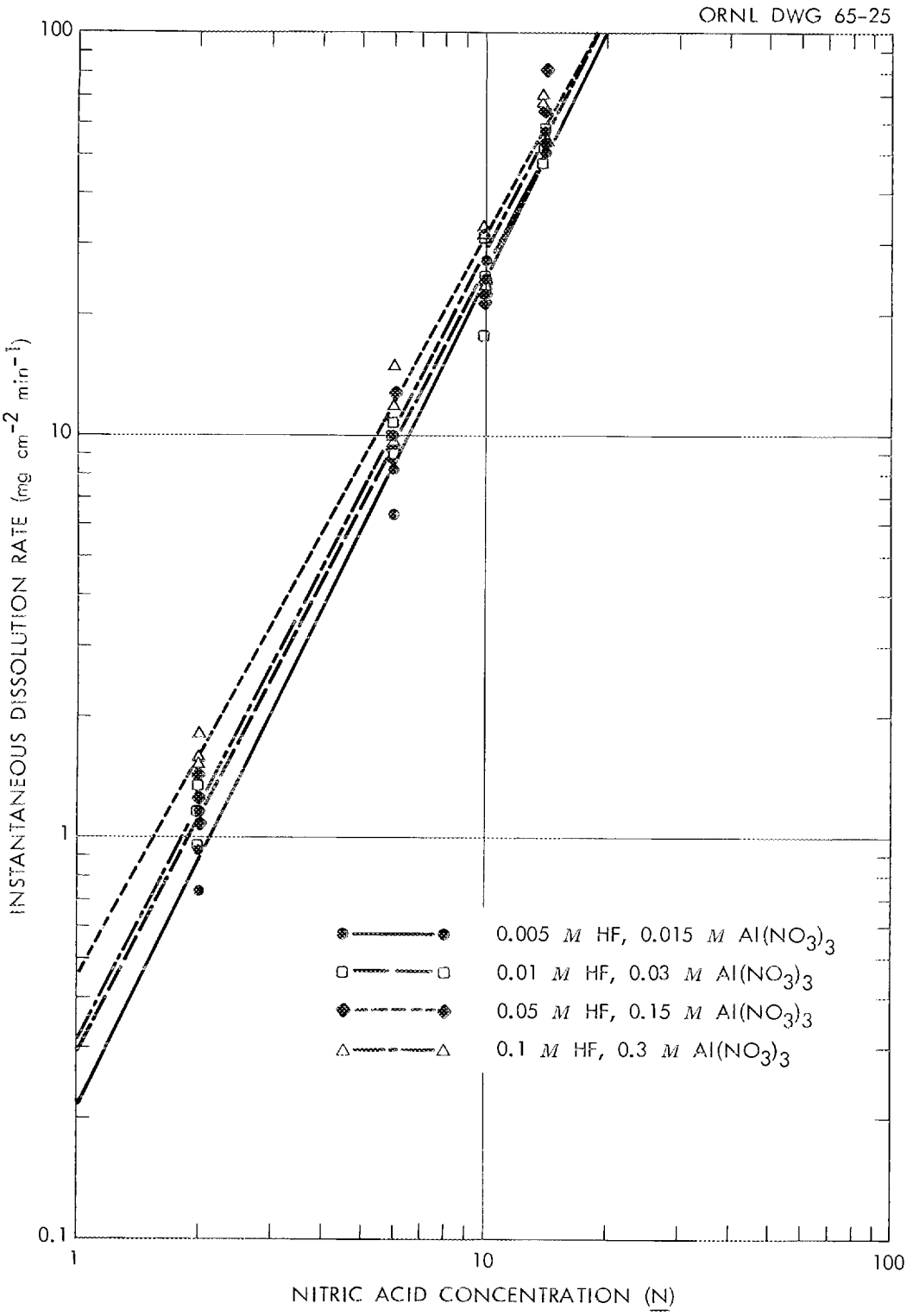


Fig. 5. Dissolution Rates of UO_2 Pellets in Nitric-Hydrofluoric Acid, and Aluminum Nitrate (M Al/M HF = 3).

solutions accounted for 0 to 80% of the total nitrate (Table A-5, Fig. 6). Taylor, et al.,[3] also showed this relationship but not over as wide a range of nitrate concentrations. Their data were obtained with monovalent nitrates only, and they reported that ammonium nitrate was an exception.

3.1.6 In HNO_3 Containing $UO_2(NO_3)_2$

The dissolution rate for UO_2 in nitric acid-uranyl nitrate solutions increased as the second power of the nitric acid plus one-half the nitrate from the uranyl nitrate (Table A-6, Fig. 7) instead of increasing as the second power of the total nitrate concentration as indicated from the data in the previous section. These experiments provide a means of calculating the decrease in rate during the complete dissolving of UO_2 fuels as follows:

$$R = C\left[\underline{M}\ HNO_3 + \underline{M}\ UO_2(NO_3)_2\right]^2, \qquad (5)$$

or

$$R = C\left[\text{initial } HNO_3 - 1/2 HNO_3 \text{ consumed}\right]^2. \qquad (6)$$

These data were obtained by physical measurements of the pellets since the small increase in uranium concentration due to the dissolution of the pellet could not be accurately determined chemically.

3.1.7 In HNO_3 Containing $NaNO_2$

Taylor[3] reported that the dissolving of UO_2 in nonboiling nitric acid was catalyzed by nitrous acid and that the addition of sodium nitrite increased the rate. In our experiments, performed with boiling solutions, this effect was not seen probably due to the rapid loss of nitrite as a result of vaporization and oxidation (Table A-7).

3.1.8 Of Varying Density

Taylor[3] also reported that the dissolution rate of UO_2 in nitric acid decreased with increasing bulk density. Our results, from pellets that had densities in the range 7.6 to 10.7 g/cm^3, were in general agreement, but we also observed wide variation in the initial instantaneous rates

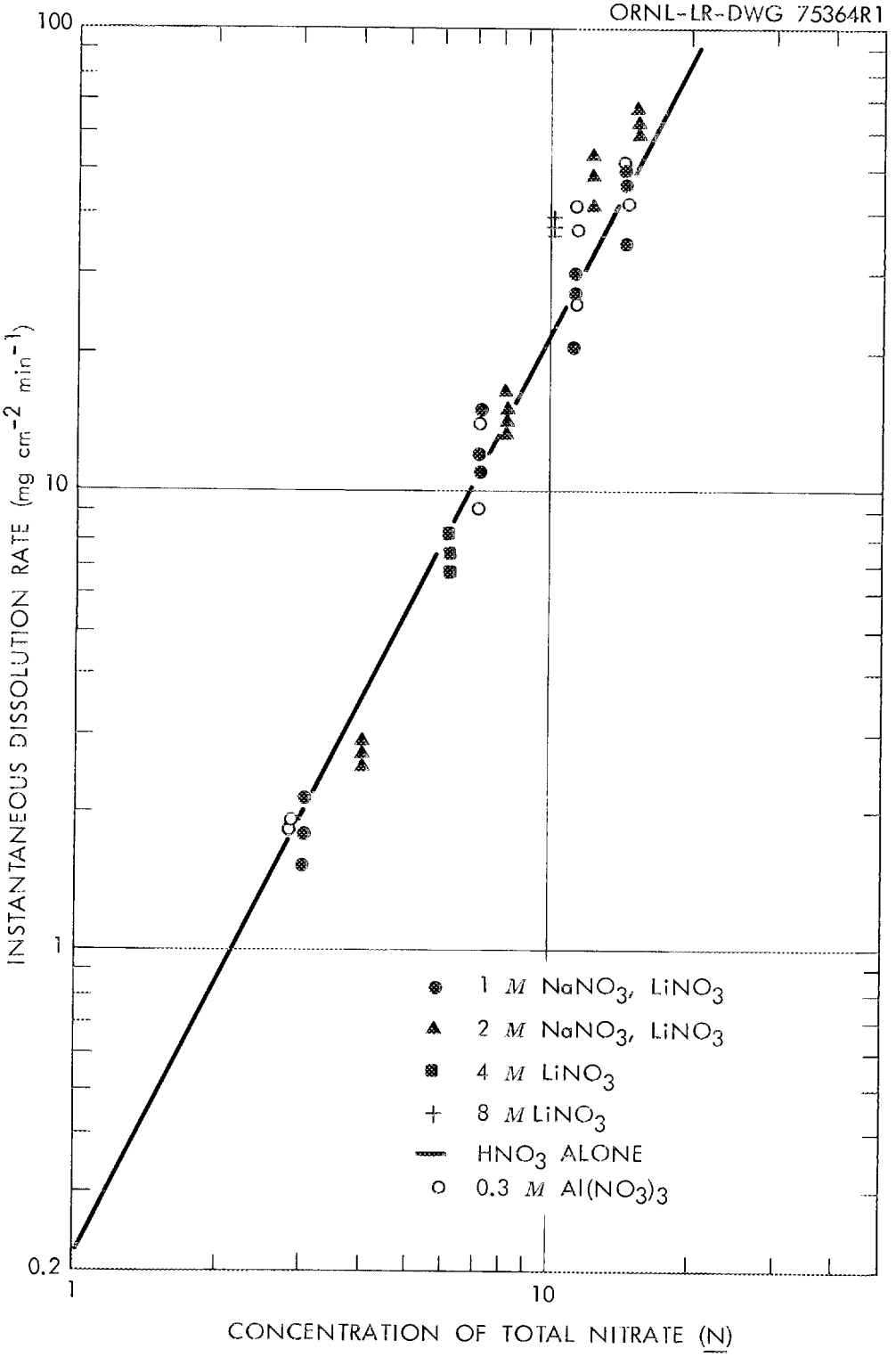


Fig. 6. Dissolution Rates of UO_2 Pellets in Nitric Acid Containing Various Nitrate Salts.

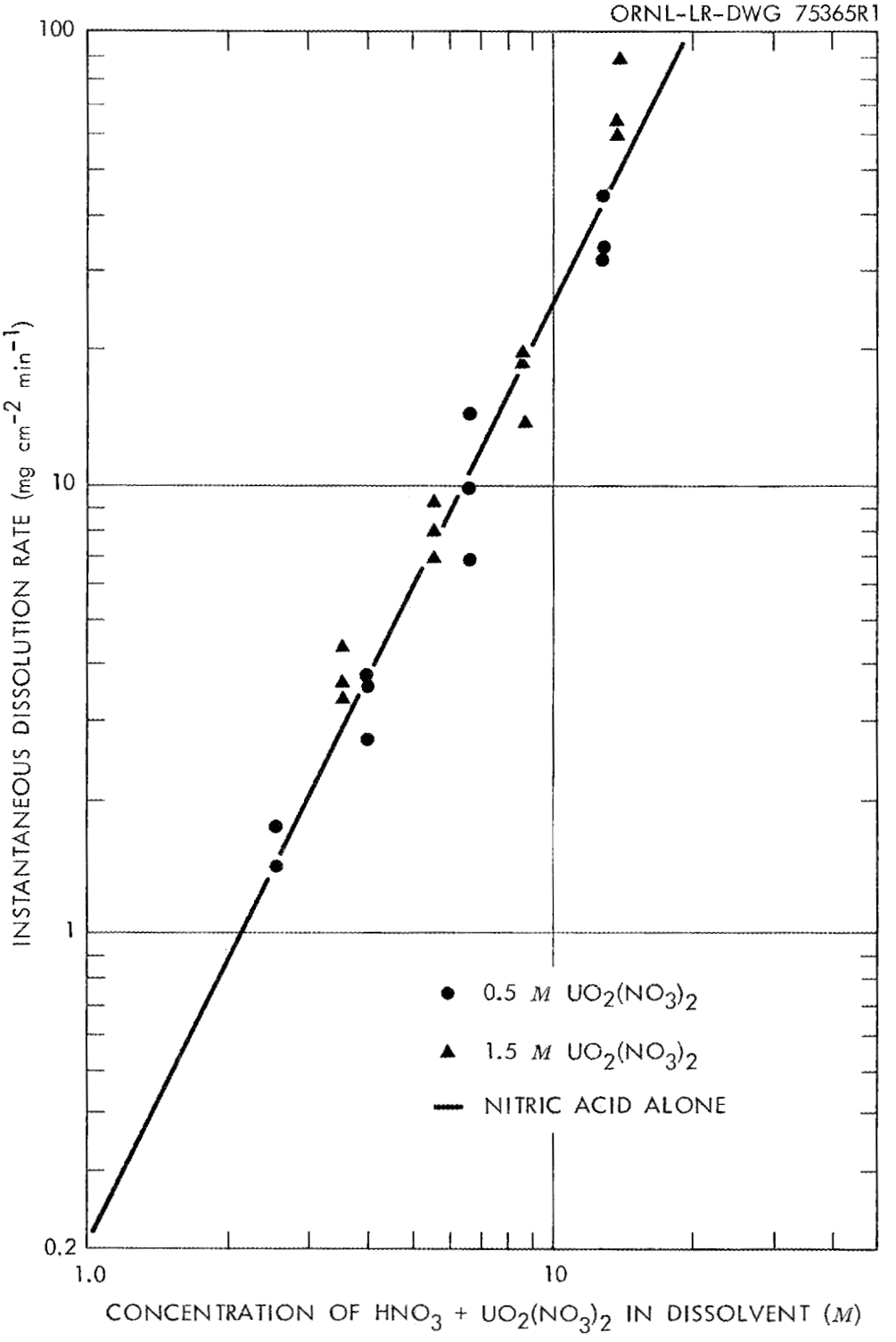


Fig. 7. Dissolution Rates of UO_2 Pellets in Nitric Acid Containing Uranyl Nitrate.

with pellets of the same density (Fig. 8, Table A-8). For example, a group of Davison pellets (densities of 10.2 to 10.4 g/cm^3) gave rates that varied from 2.0 to 50.0 mg UO_2 cm^{-2} min^{-1} when dissolved in 6 M HNO_3. (See Sec 5.2.3 for data on complete dissolving of these pellets.) More consistent data were obtained with pellets from other sources. The equation determined from a least-squares fit of this data is: IDR = $1.74 \times 10^4 \, e^{-0.091 \, (\% \, TD)}$, where (% TD) is the density of the pellet, expressed as percentage of the theoretical.

Three parameters were considered in an attempt to correlate these rate data: oxygen-to-uranium ratio in the pellets, pore volume by mercury penetration, and estimates of surface area by metallographic examination. The oxygen-to-uranium ratio of all pellets was nearly the same, and no correlation with the dissolution rate could be made. The pore volume by mercury penetration varied from 1 to 10% and did not correlate with the increased IDR of the pellets. Metallography showed that the surface area of the pellets agreed at least qualitatively with the variation in rate (Fig. 9). No method was found to give the actual surface area of single pellets.

In spite of the wide variation in dissolution rates of different pellets, the rate for all pellets was proportional to the square of the nitric acid concentration (Fig. 10). This effect is independent of initial surface area and is apparently independent of rate of change of surface area during dissolution. The equation for variation in rate with density and nitric acid (using the line shown in Fig. 8) is:

$$IDR_{UO_2} = (HNO_3)^2 \, 480 \, e^{-0.091 \, (TD)} \quad . \qquad (7)$$

Much of the wide variation in data in Fig. 8 is undoubtedly due to variation in surface area. Since surface area could not be accurately determined and was not included in Eq. (7), predictions of initial instantaneous dissolution rates using this equation for a given set of pellets may be inaccurate by a factor of 50 in exceptional cases. However, the rate during the dissolution of the bulk of the pellet may be predicted to within about 50% of the experimental value. Accurate data may be

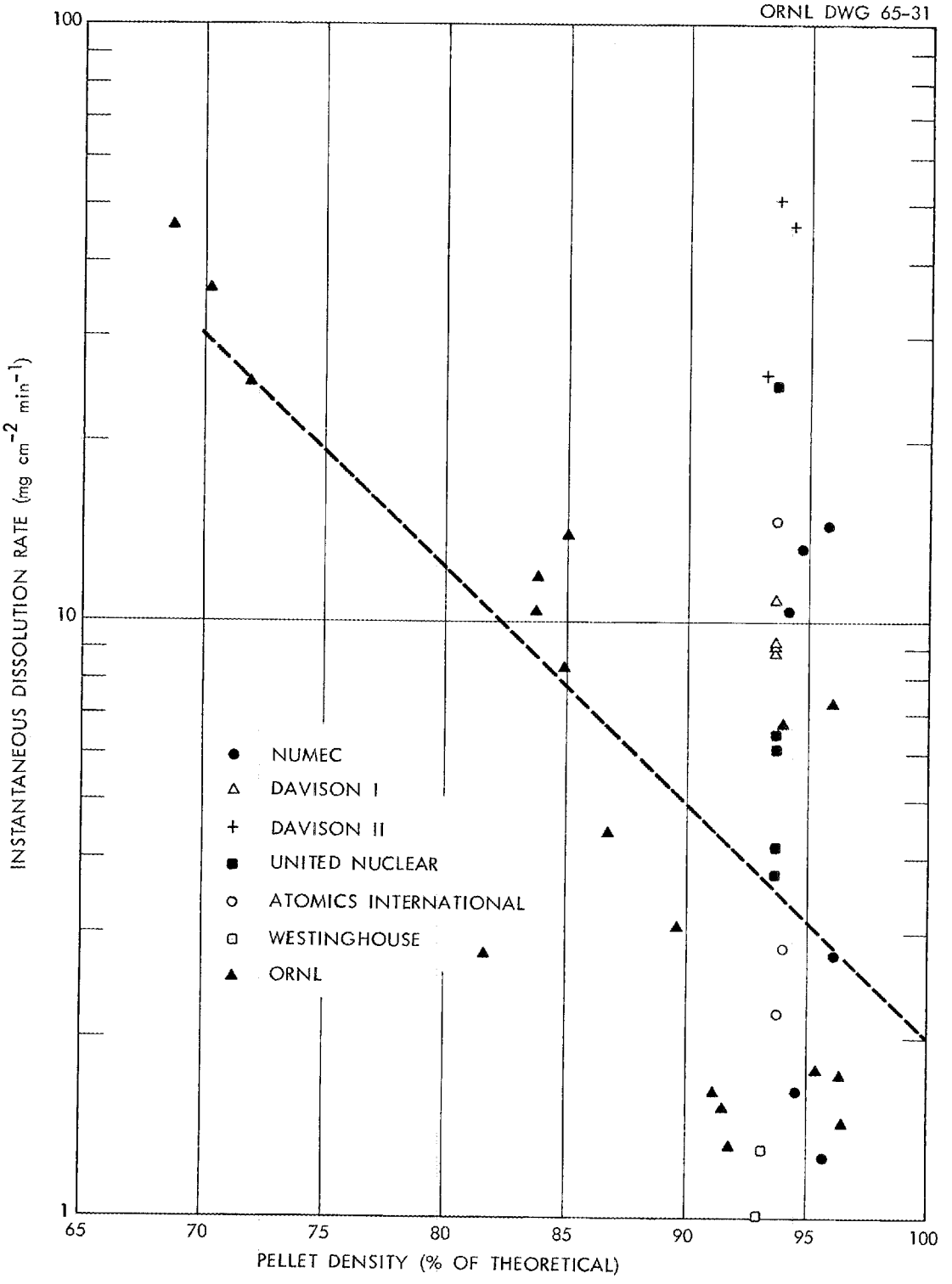
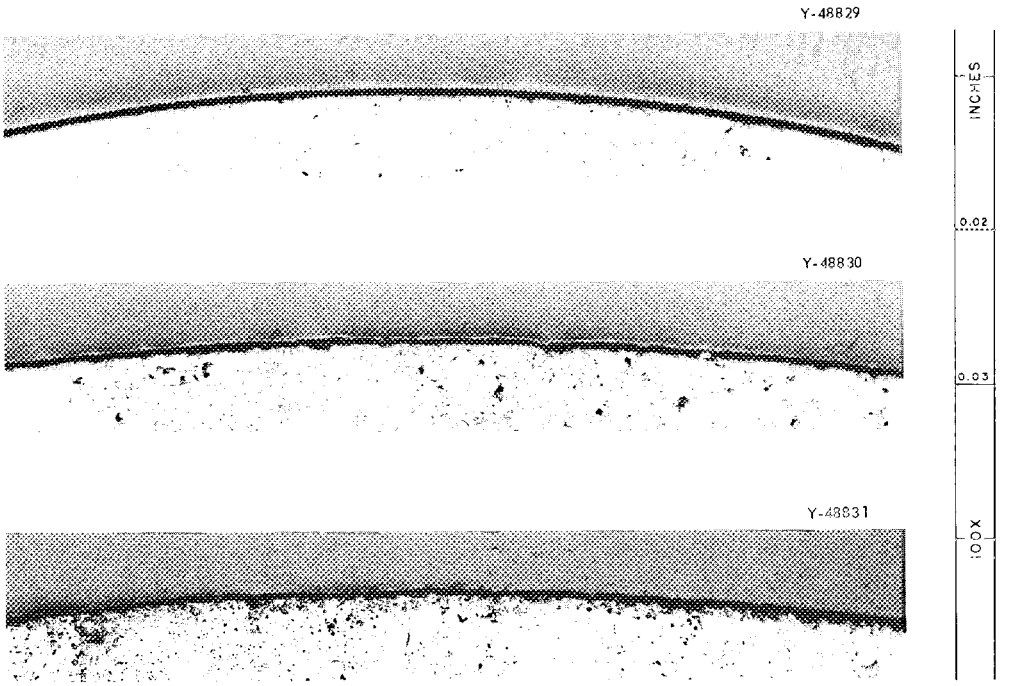
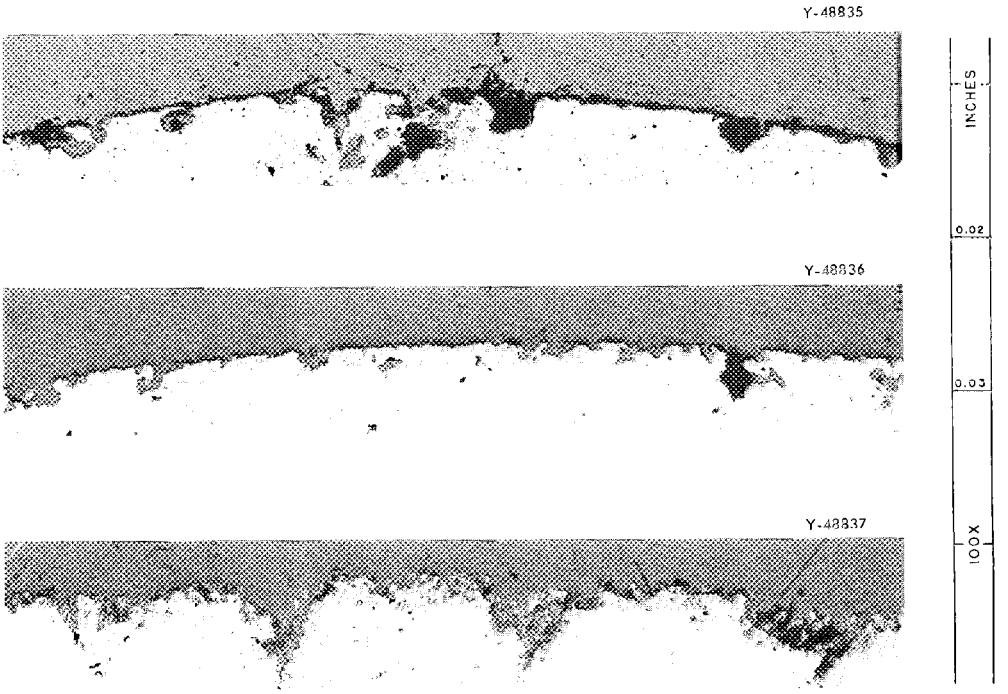


Fig. 8. Effect of Density on Dissolution Rates of UO_2 Pellets in 6 M HNO_3.



EDGE OF PELLETS BEFORE DISSOLUTION



EDGE OF PELLETS AFTER INITIAL DISSOLUTION

Fig. 9. Metallographic Sections of UO_2 Pellets Before and During Dissolution.

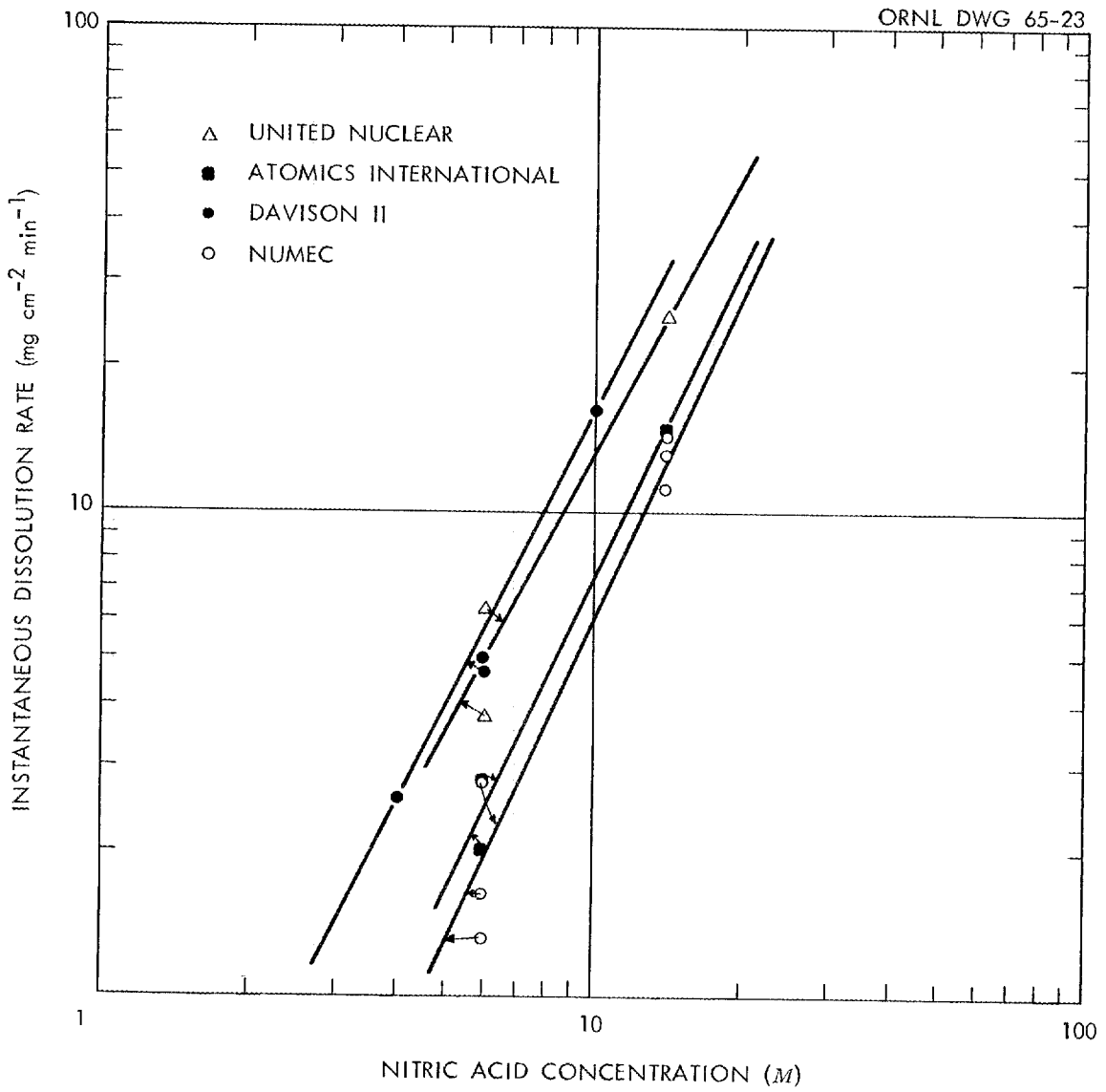


Fig. 10. Effect of Nitric Acid Concentration on Dissolution Rates of UO_2 Pellets from Various Sources.

obtained by use of the appropriate experimentally determined constant for the pellets of interest.

3.2 Dissolution Rates of Sintered PuO_2 Pellets

The dissolving of PuO_2 with boiling mixtures of nitric and hydrofluoric acid has been previously reported,[6] but those studies were made with PuO_2 powder or powder compacts, whereas present interest is focused on sintered pellets. Our studies also included the use of the variety of reagents used in the study of UO_2 dissolution rates (Sec 4.1). Since the dissolution rate of the PuO_2 was low with all these reagents except with highly corrosive HNO_3-HF solutions, other additives were also investigated. Solvents included boiling nitric acid, mixtures of nitric acid-hydrofluoric acid, nitric acid-hydrofluoric acid-aluminum nitrate, nitric acid-monovalent nitrates (sodium or lithium nitrate), and nitric acid containing several oxidants, including sodium dichromate, ceric ions, ozone, and peroxide. Since aqua regia may be used to declad stainless steel elements (Darex), the dissolution rate in this reagent was investigated. The effect of pellet density was also studied.

3.2.1 In HNO_3

The instantaneous dissolution rate of PuO_2 in boiling 7, 10, and 14 $\underline{M}$ HNO_3 was less than 10^{-2} mg cm^{-2} min^{-1} (Table A-9). The logarithmic plot is linear (Fig. 11) and fits the equation: $R = 1.1 \times 10^{-7} (\underline{M}\ HNO_3)^4$.

3.2.2 In HNO_3-HF

Adding fluoride to the nitric acid greatly increased the dissolution rate. The results obtained with 7, 10, and 14 $\underline{M}$ HNO_3 containing 0.005, 0.01, 0.05, and 0.1 $\underline{M}$ HF are given in Table A-9. The rate of PuO_2 remained proportional to the fourth power of the nitric acid concentration (Fig. 11) and was proportional to the HF concentration raised to the 1.4 power (Fig. 12). For these particular pellets the rate can be expressed by the equation:

$$R_{PuO_2} = 1.1 \times 10^{-7} (\underline{M}\ HNO_3)^4 + 9.2 \times 10^{-4} (\underline{M}\ HNO_3)^4 (\underline{M}\ HF)^{1.4} . \quad (8)$$

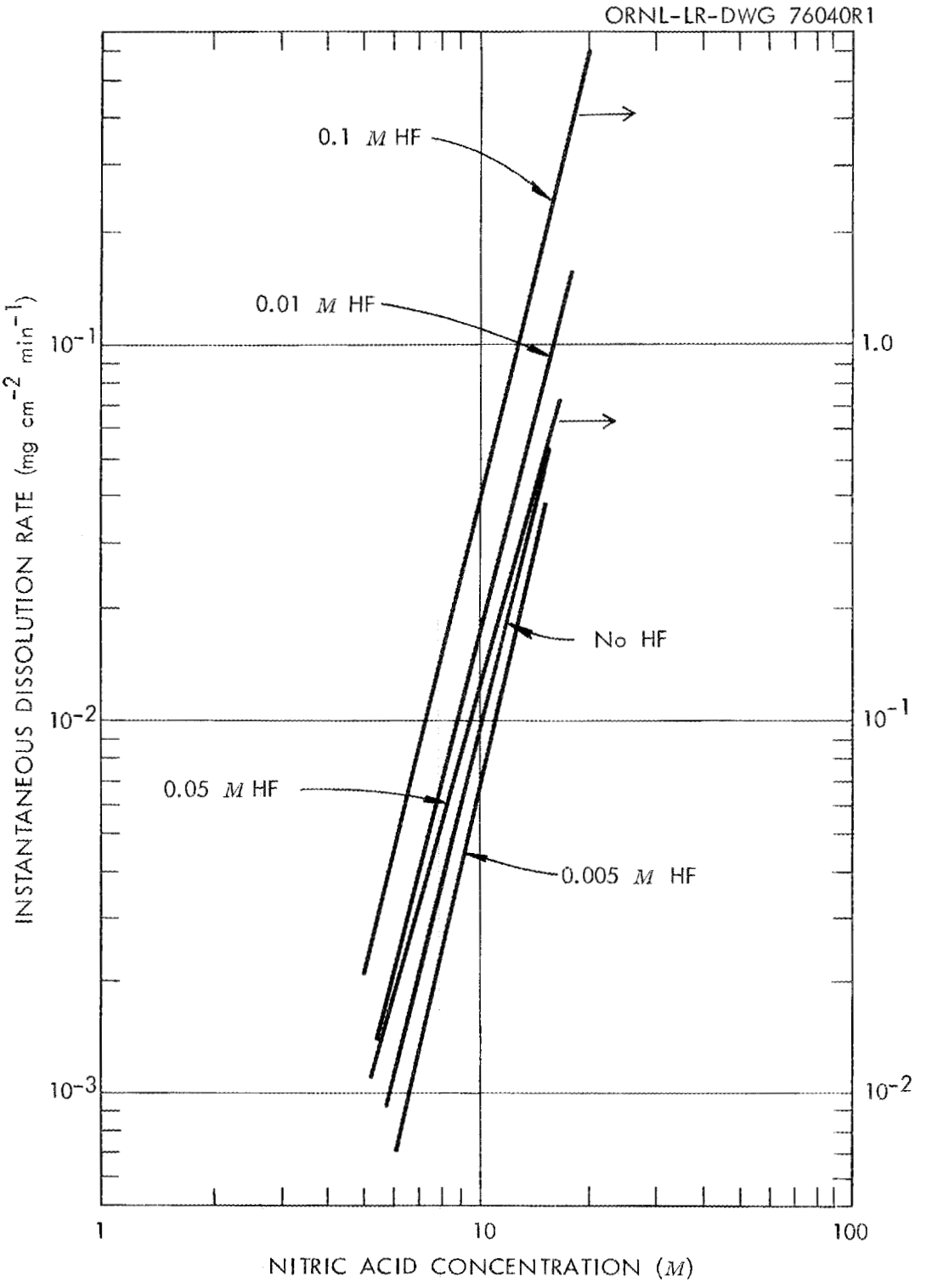


Fig. 11. Effect of Nitric Acid Concentration on the Rate of Dissolution of PuO_2 Pellets in Nitric-Hydrofluoric Acid Solutions.

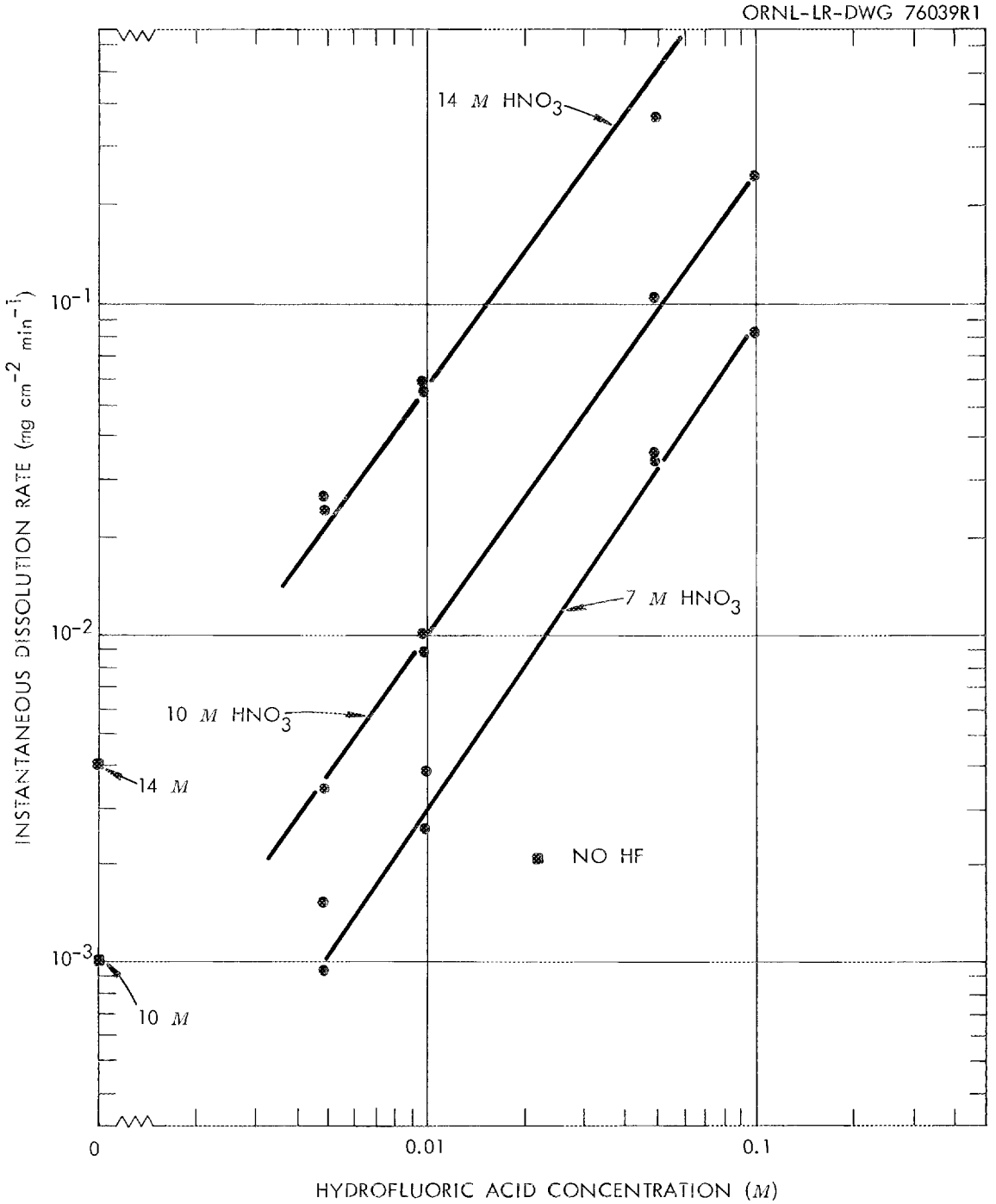


Fig. 12. Effect of Hydrofluoric Acid Concentration on the Rates of Dissolution of PuO_2 Pellets in Nitric-Hydrofluoric Acid Solutions.

3.2.3 In HNO_3-HF-$Al(NO_3)_3$

As was observed with UO_2 pellets, adding three moles of aluminum nitrate per mole of fluoride practically negates the effect of the fluoride (Table A-9). These data indicated that the instantaneous rate for PuO_2 remained proportional to the fourth power of the nitric acid concentration (Fig. 13) and to the concentration of complexed fluoride raised to the 0.36 power (Fig. 14). An approximate empirical equation for calculating the dissolution of the PuO_2 in this mixture is:

$$R = 1.1 \times 10^{-7} (\underline{M}\ HNO_3)^4 + 4.8 \times 10^{-7} (\underline{M}\ HNO_3)^4 (\underline{M}\ HF_{Al})^{0.36}, \qquad (9)$$

where ($\underline{M}\ HF_{Al}$) is the concentration of hydrofluoric acid complexed with aluminum nitrate. The great decrease in the rate when aluminum is added to complex the fluoride is indicated in the 500-fold reduction of the constant in the second term. The rapid decrease in rate may be seen by the following series of experiments. The rate increased from 1×10^{-3} mg cm^{-2} min^{-1} in 10 $\underline{M}$ HNO_3 to 2.7×10^{-1} in 10 $\underline{M}$ HNO_3--0.1 $\underline{M}$ HF; then it is decreased to 6.6×10^{-3}, 4.7×10^{-3}, and 4.1×10^{-3}, respectively, as 1, 2, and 3 moles of aluminum nitrate per mole of fluoride were added to the solution (Fig. 15).

3.2.4 In HNO_3-Ce(IV)

A patent was issued at Hanford[11] for a process for dissolving PuO_2 powder in nitric acid containing cerium ions. We studied this system with our pellets by adding the cerium as ceric ammonium nitrate $[Ce(NH_4)_2(NO_3)_6]$. With 0.005 to 0.1 $\underline{M}$ Ce(IV) in 4 $\underline{M}$ HNO_3, the dissolution rate was approximately proportional to the first power of the ceric ion concentration (Table A-10, Fig. 16). At lower Ce(IV) concentrations, the rates were the same as those in nitric acid alone.

The rate also increased with ceric ion concentration in 2 $\underline{M}$ HNO_3 but in 7, 10, and 14 $\underline{M}$ HNO_3 the rate was the same as in the acid alone.

Although there was some increase in rate with this system, the rate remained too low for practical application. There is an indication that the ceric ion was reduced too rapidly at the higher acidities to be effective.

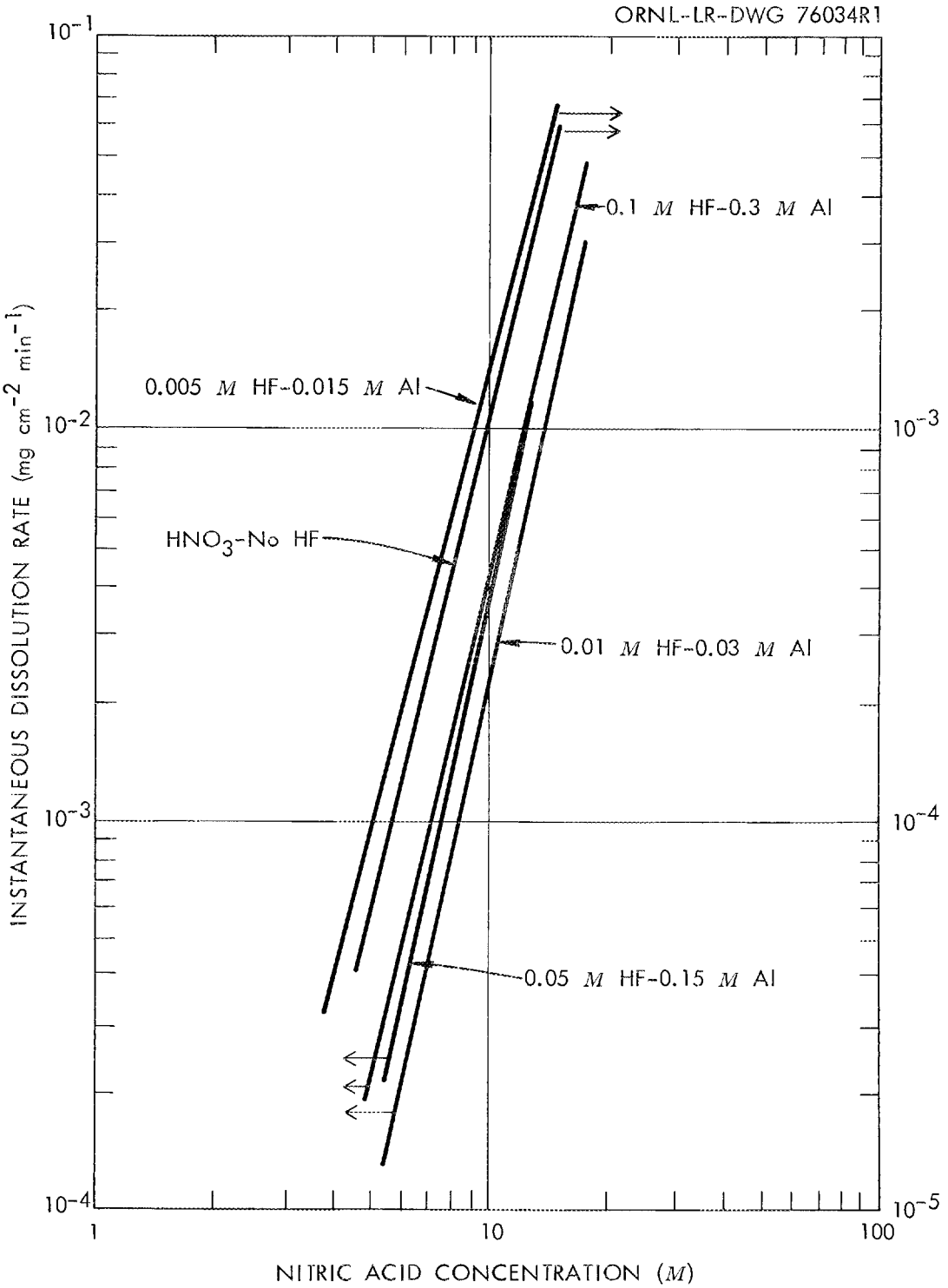


Fig. 13. Effect of Nitric Acid Concentration on the Rate of Dissolution of PuO_2 Pellets in Nitric Acid-Hydrofluoric Acid-Aluminum Nitrate Solutions.

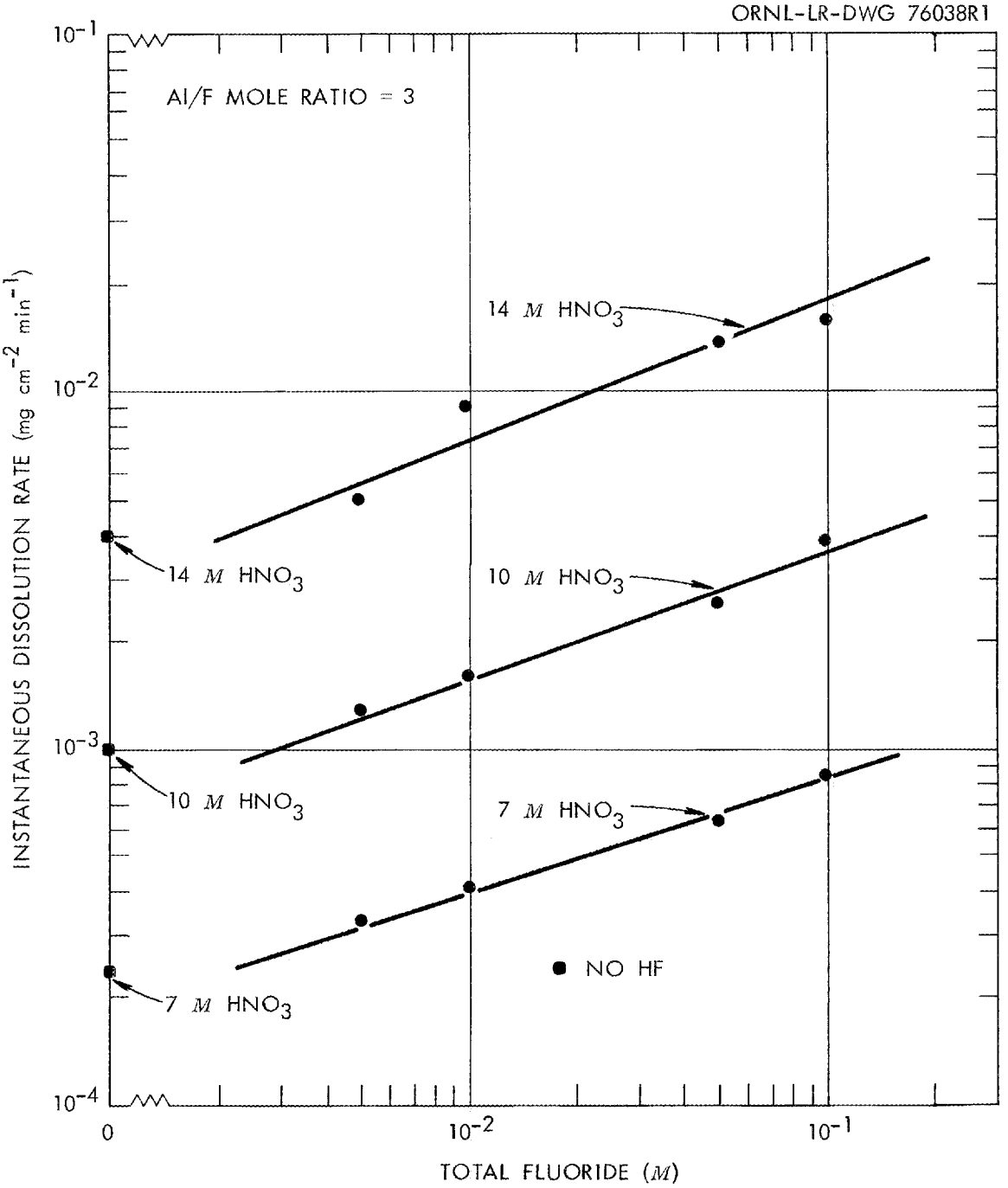


Fig. 14. Effect of Hydrofluoric Acid Concentration on the Rate of Dissolution of PuO_2 Pellets in Nitric Acid-Hydrofluoric Acid-Aluminum Nitrate Solutions.

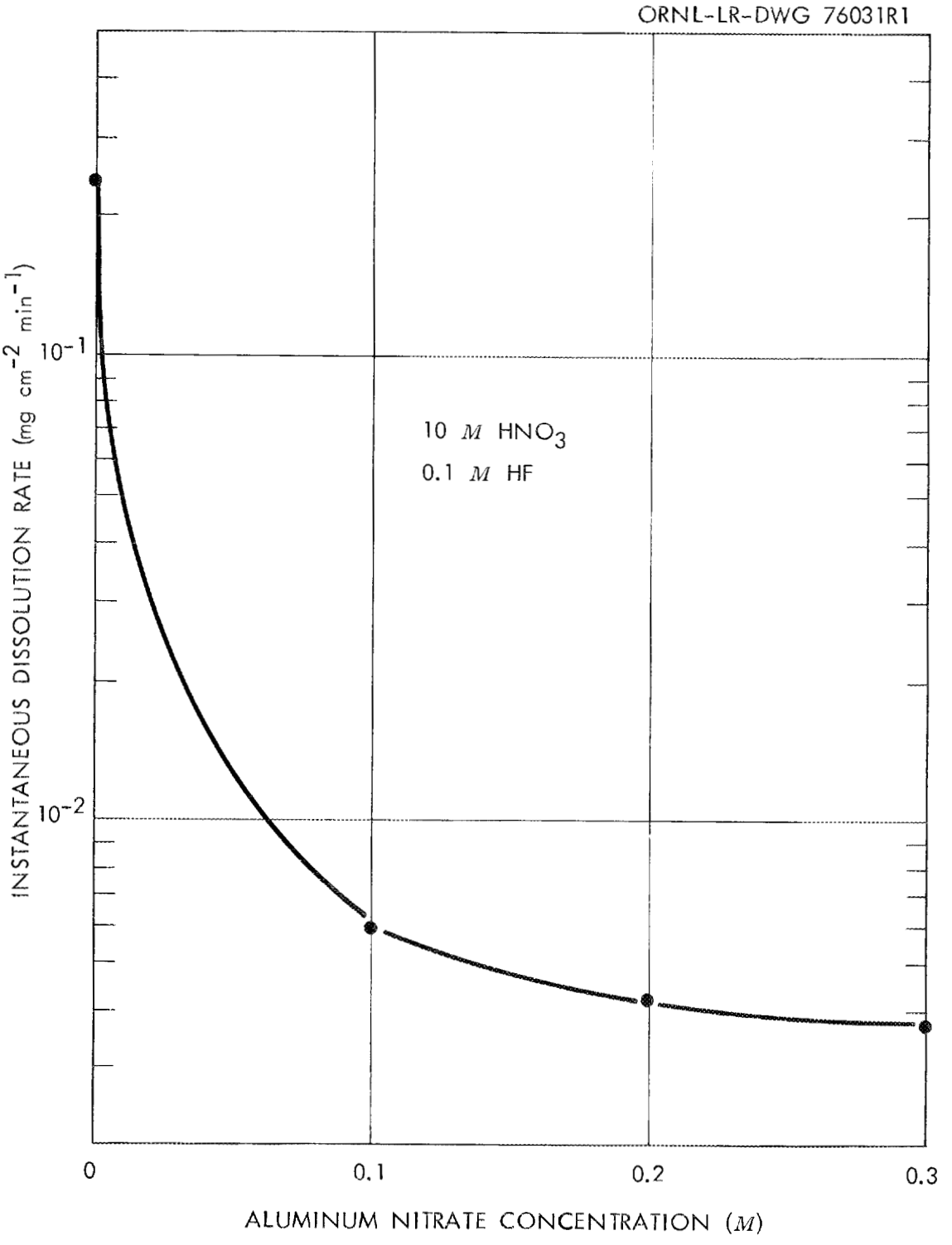


Fig. 15. Effect of Aluminum Nitrate Concentration on the Rate of Dissolution of PuO_2 Pellets in Nitric Acid-Hydrofluoric Acid-Aluminum Nitrate Solutions.

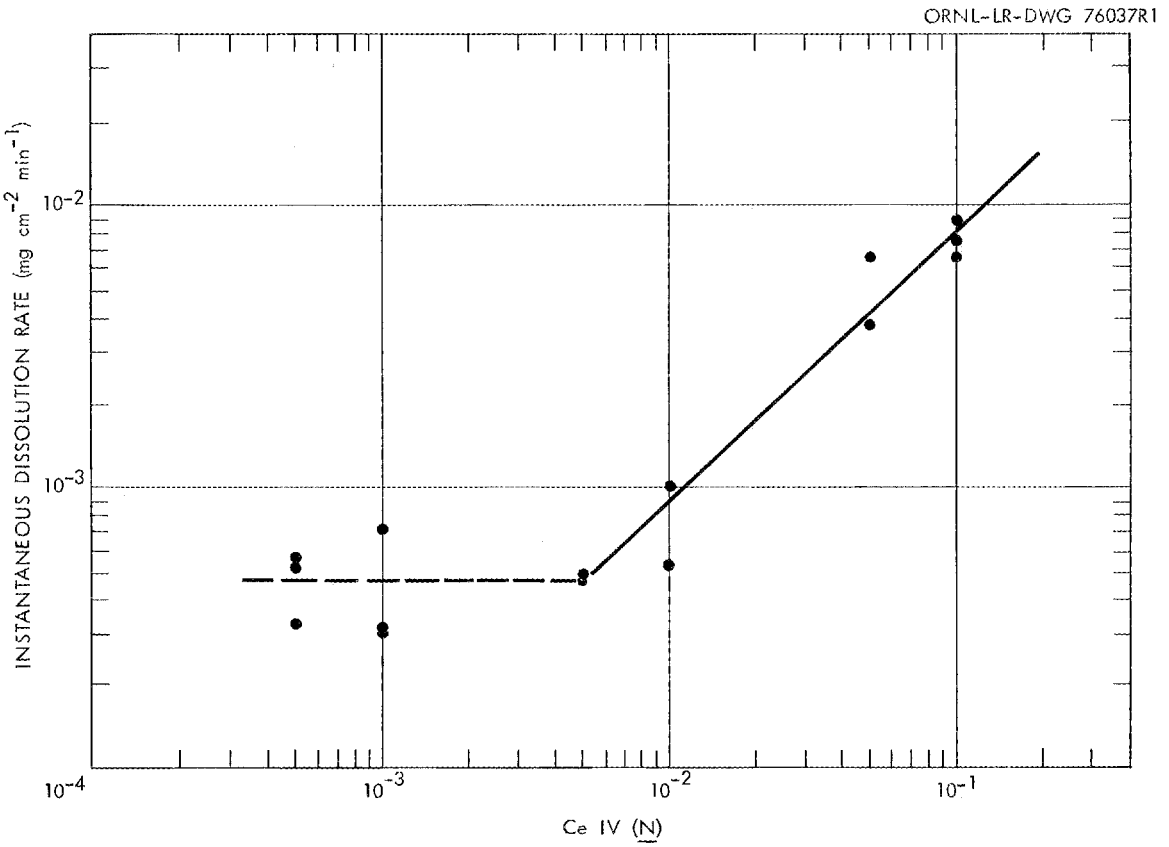


Fig. 16. Effect of the Ceric Concentration on the Dissolution Rate of PuO_2 in 4 N HNO_3-$Ce(NH_4)_2(NO_3)_6$.

3.2.5 In HNO_3-O_3

Since the rate increased with ceric ion, experiments were made with ozone as the oxidizing agent. The ozone was obtained with a laboratory ozonator (Welsbach Corporation, Philadelphia, Pa.). At 8-psig oxygen, this instrument delivered 6% ozone. First, the effect of the ozone flow rate was studied in 7 M HNO_3. At all flow rates (Table A-11) the dissolution rate was the same as that with nitric acid alone. Similarly, with 0.04 ft^3/min flow rate (6% O_3--94% O_2), dissolution rates in 7 to 14 M HNO_3 were the same as those obtained with nitric acid alone. However, when ozone was added to 2 N HNO_3, the rate increased and was greater than with 7 M HNO_3 alone. The rate remained impractically low, however. As with ceric ion (above), these results are probably due to the instability of ozone at high acidities.

3.2.6 In HNO_3-H_2O_2

Experiments with 7 M HNO_3 to which hydrogen peroxide was added at different flow rates show that the dissolution rate for PuO_2 does not increase over that with nitric acid alone.

3.2.7 In HNO_3-$Na_2Cr_2O_7$

Inclusion of 0.1 N $Na_2Cr_2O_7$ in 7, 10, and 14 M HNO_3 did not increase the rate, compared with that for nitric acid alone.

3.2.8 In HNO_3 Containing $NaNO_3$ or $LiNO_3$

Contrary to the results with UO_2, increasing the total nitrate concentration by adding 1 to 4 M sodium or lithium nitrate to 7 M HNO_3 did not influence the rate.

3.2.9 In HNO_3-HCl

The Darex process, which may be used to declad stainless-steel-clad ThO_2 fuels, may be used equally as well to declad PuO_2 clad in stainless steel. The maximum instantaneous dissolution rate of PuO_2 pellets in a mixture of 3 to 10 M HNO_3 and 0.1 to 5 M HCl was about 10^{-3} mg cm^{-2} min^{-1} (Table A-12).

3.2.10 Of Varying Density

The dissolution rate of PuO_2 pellet decreased exponentially with increase in pellet density over the limited range of densities available in test specimens, i.e. 8.86 to 10.38 g/cm^3 (Table A-13, Fig. 17).

The dissolution rate in 14 $\underline{M}$ HNO_3 varied from 1.36×10^{-1} to 3.90×10^{-3} mg cm^{-2} min^{-1}. An equation fitting this data is:

$$IDR = 2.38 \times 10^{8}\ e^{-0.272\ (\%\ TD)}\ , \qquad (10)$$

where (% TD) is the % of theoretical density.

This equation together with Eq. (9) gives the relation:

$$IDR = 5 \times 10^{3}\ (\underline{M}\ HNO_3)^{4}\ e^{-0.27\ (\%\ TD)}$$
$$+ 4 \times 10^{7}\ (\underline{M}\ HNO_3)^{4}\ (\underline{M}\ HF)^{1.4}\ e^{-0.27\ (\%\ TD)}\ , \qquad (11)$$

from which the IDR of PuO_2 pellets of 75 to 93% theoretical density in 4 to 14 $\underline{M}$ HNO_3 and 0 to 0.1 $\underline{M}$ HF were calculated to within about 50% of the experimental value.

3.3 Dissolution Rates of Sintered PuO_2-UO_2 Pellets

The dissolution rate of PuO_2-UO_2 pellets is dependent upon the ratio of plutonium to uranium and the method of fabrication of the pellet (see Sec 3), in addition to dissolvent composition and pellet density as described previously for pure UO_2 and PuO_2.

The pellets used in the rate experiments described in the following sections were true solid solutions based on the nitric acid solubility test.

3.3.1 Of Varying PuO_2 Concentration

The theoretical density of UO_2-PuO_2 solid solutions was calculated from the equation:

$$TD_{PuO_2\text{-}UO_2} = n(11.44) + (1-n)(10.98)\ , \qquad (12)$$

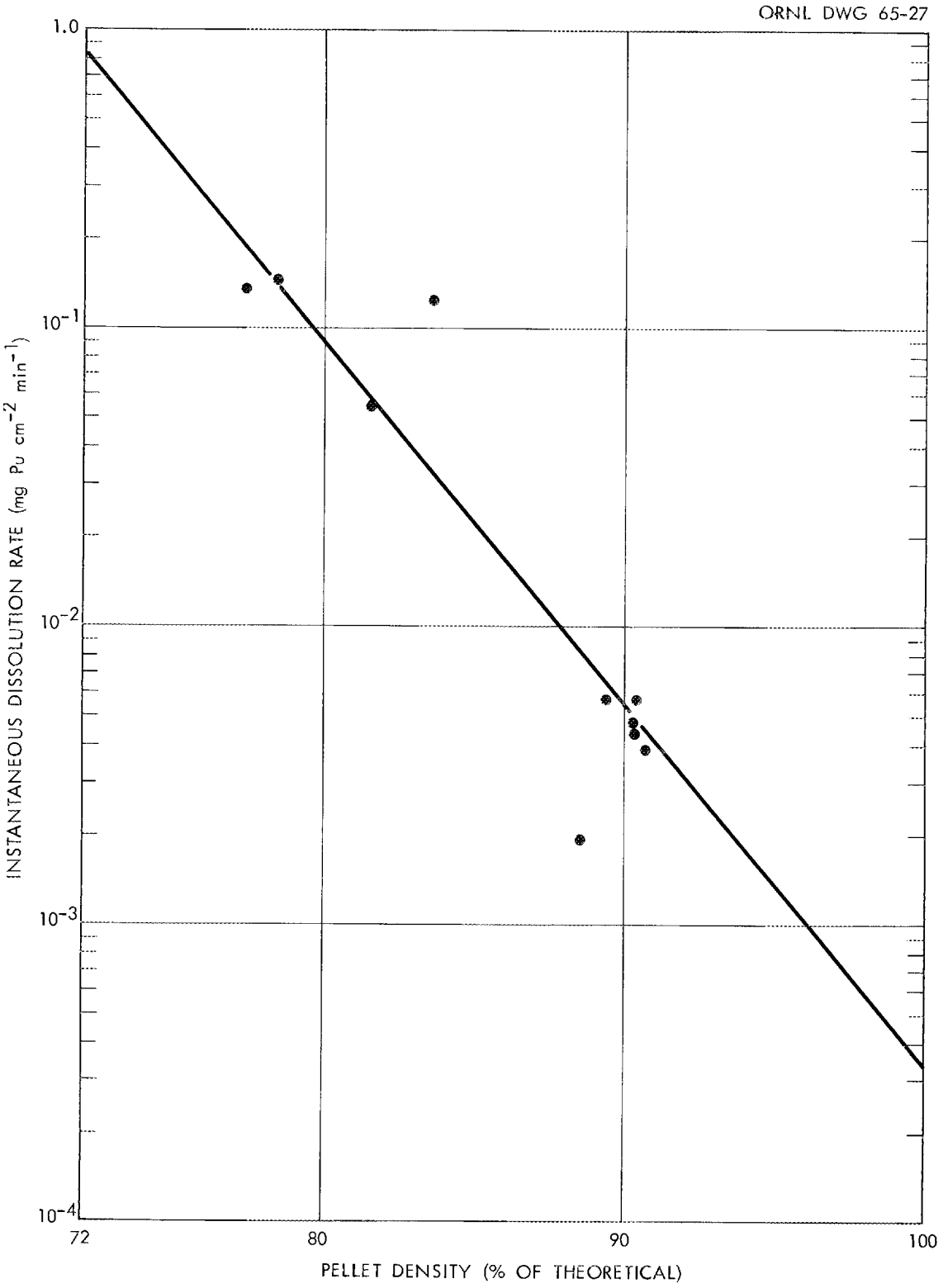


Fig. 17. Dissolution Rates of PuO_2 Pellets of Varying Density (14 N HNO_3).

where n is the mole fraction of PuO_2 in the mixture. This equation is valid due to the almost ideal solid solution formed in this system.

Instantaneous dissolution rate studies showed that the rate for high-density PuO_2-UO_2 pellets is proportional to the mole fraction of PuO_2 in the solid solution and may be calculated by the equation:

$$IDR_{PuO_2-UO_2} = IDR_{PuO_2}{}^{n}\ IDR_{UO_2}{}^{1-n}\ , \qquad (13)$$

where n is the mole fraction of PuO_2 in the solid solution (Fig. 18). The rates for the instantaneous dissolution in the solvent were determined for PuO_2 and UO_2 of the same density as that of the mixture. For example, the IDR of 20% PuO_2--80% UO_2 (density 8.9) in 7 M HNO_3 may be calculated as follows:

$$\%\ TD_{PuO_2-UO_2} = \frac{8.9 \times 100}{0.20\ (11.44) + 0.80\ (10.98)} = 80.4\%\ ,$$

$$IDR_{PuO_2} = 5 \times 10^3\ e^{-0.27\ (80.4)}\ (7)^4 = 1.04 \times 10^{-2}\ mg\ cm^{-2}\ min^{-1}\ ,$$

$$IDR_{UO_2} = 483\ e^{-0.091\ (80.4)}\ (7)^2 = 15.9\ mg\ cm^{-2}\ min^{-1}\ ,$$

$$IDR_{PuO_2-UO_2} = (1.04 \times 10^{-2})^{0.2}\ (15.9)^{0.8} = 3.67\ mg\ cm^{-2}\ min^{-1}\ ,$$

This value is about 30% less than the experimental value of 5.7 mg cm^{-2} min^{-1}.

3.3.2 In HNO_3

As previously shown, the dissolution rates for PuO_2 and UO_2 are respectively proportional to the second and fourth powers of the concentration of nitric acid. Substitution of these powers into Eq. (13) would indicate a rate dependence on nitric acid concentration of:

$$R_{PuO_2-UO_2} = K(HNO_3)^{2+2n}\ . \qquad (14)$$

Experimental data have confirmed this relationship (Fig. 19).

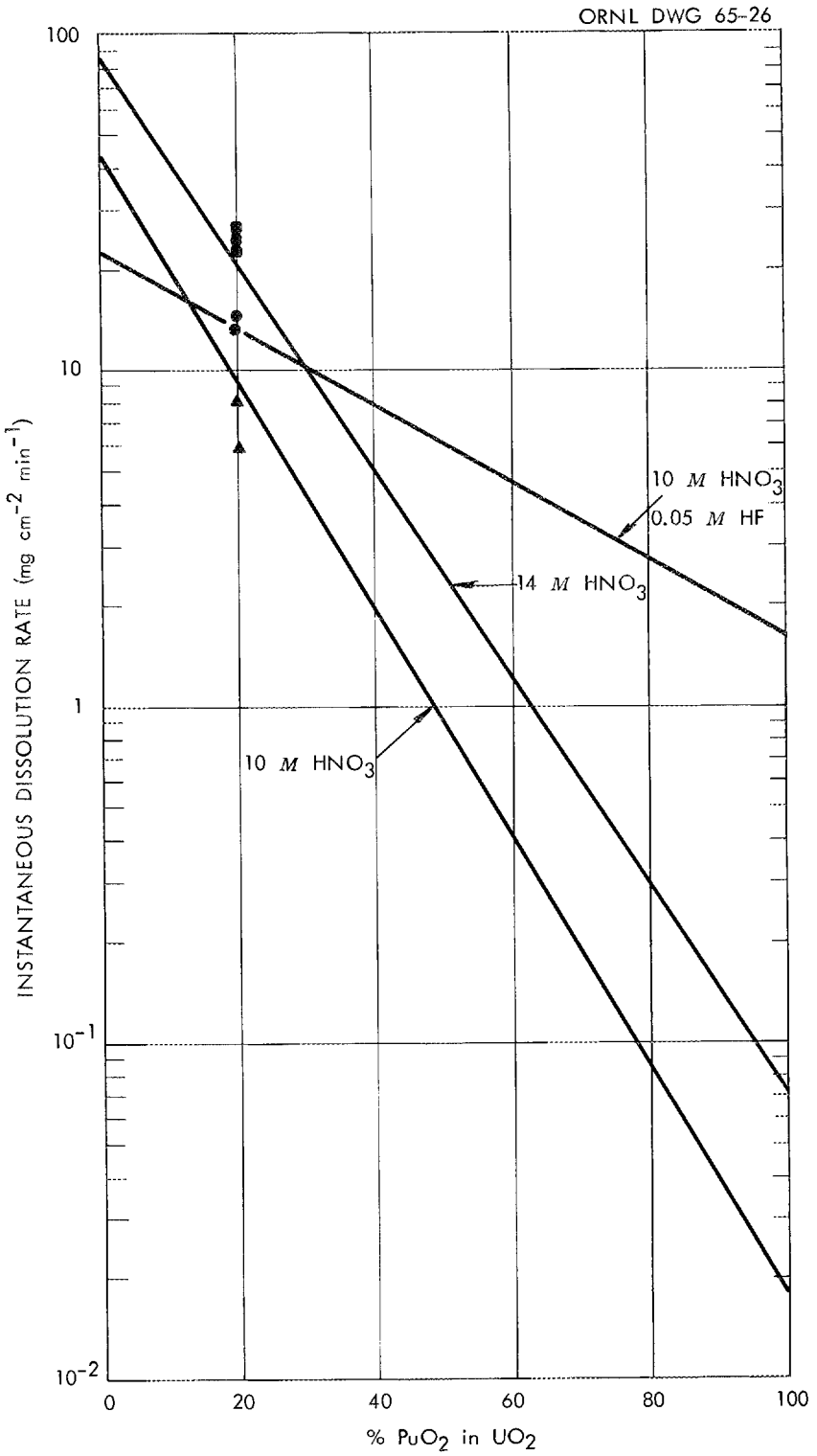


Fig. 18. Effect of Composition on the Dissolution Rates of PuO_2-UO_2 Pellets.

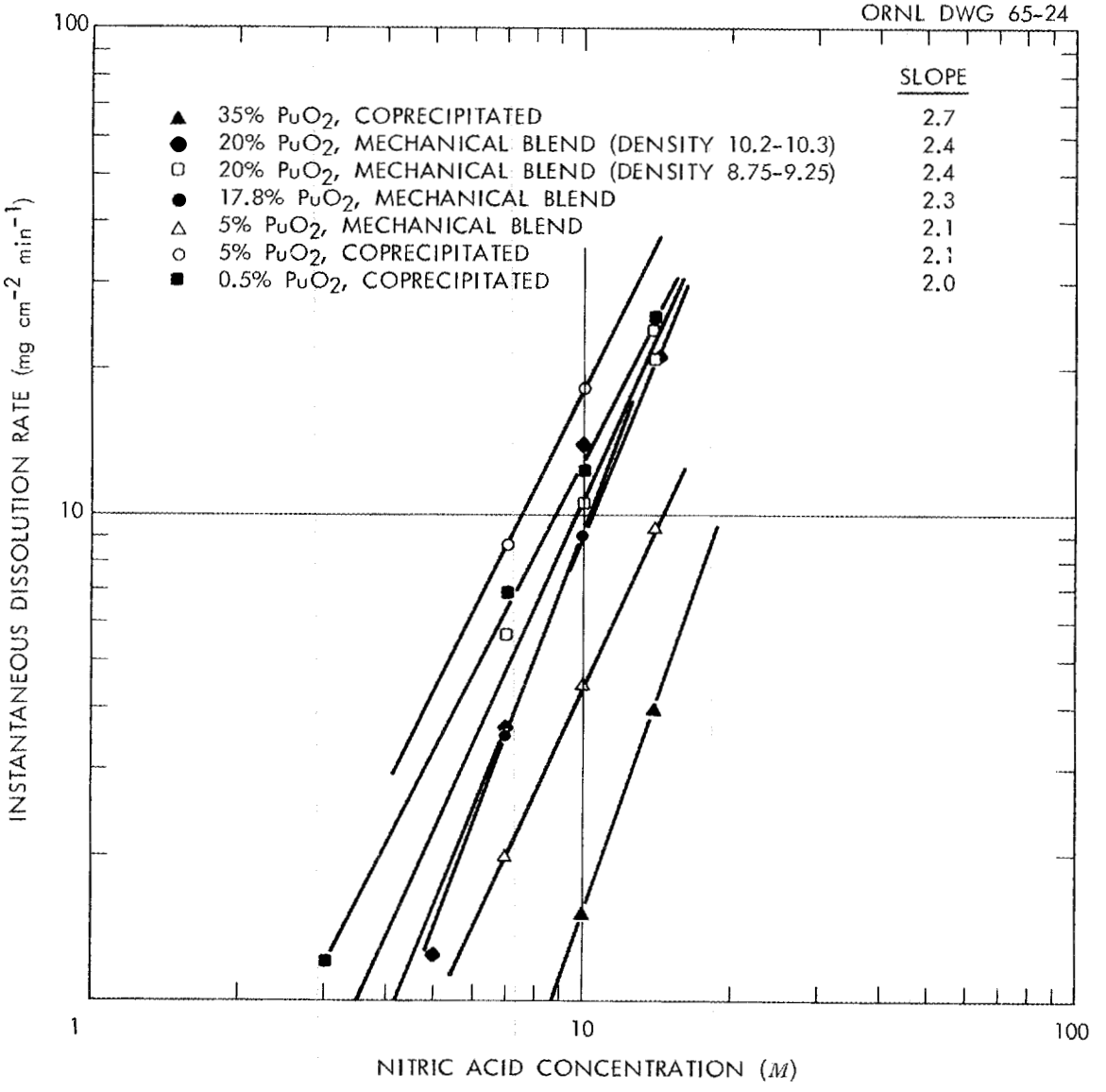


Fig. 19. Effect of Composition on the Nitric Acid Dependence of the Dissolution Rates of PuO_2-UO_2 Pellets.

4. TIME REQUIRED TO DISSOLVE PELLETS COMPLETELY

4.1 Theoretical Dissolution Time

4.1.1 Of Smooth Pellets

If all the surfaces of a smooth right cylinder dissolved at a uniform rate, the time for achieving complete solution would be the shorter time given by the equations:

$$t_{D \rightarrow 0} = \frac{D_o \rho}{2(IDR)} \text{ or } t_{L \rightarrow 0} = \frac{L_o \rho}{2(IDR)} , \qquad (15)$$

depending upon whether the diameter or the length of the pellet is the smaller dimension. Here D_o and L_o are the original diameter and length of the pellets, respectively, and ρ is density in mg/cm^3. The time to reduce the pellet to a given mass (m) is given by the equation:

$$m = \frac{\pi\rho}{4} \left[D_o^2 L_o - (2D_o L_o + D_o^2)Jt + (2D_o + 1)J^2 t^2 - J^3 t^3 \right] , \qquad (16)$$

where J is $\frac{2IDR}{\rho}$.

From the above equation, FORTRAN codes have been prepared for the calculation of the height or radius and the surface after varying amounts of the pellet have dissolved (Appendix II). Examples of the variation of these quantities during the dissolution are given in Fig. 20.

4.1.2 Roughening-Factor Calculations

The surfaces of the pellets do not dissolve uniformly, and to determine the actual time required to dissolve the pellets it is necessary to know the variation in the actual surface area as the pellet dissolves. Since we could not measure the true surface area of individual pellets (see Sec 4.1.8), we assumed that the initial surface of the pellet was the same as its geometric area and that the dissolution rate was constant. For this reason our calculations of the dissolution time are empirical. A roughening factor (RF) of the pellet was then calculated by dividing the amount of material dissolved per unit of time by the amount which would have dissolved if the surface remained smooth and the rate constant.

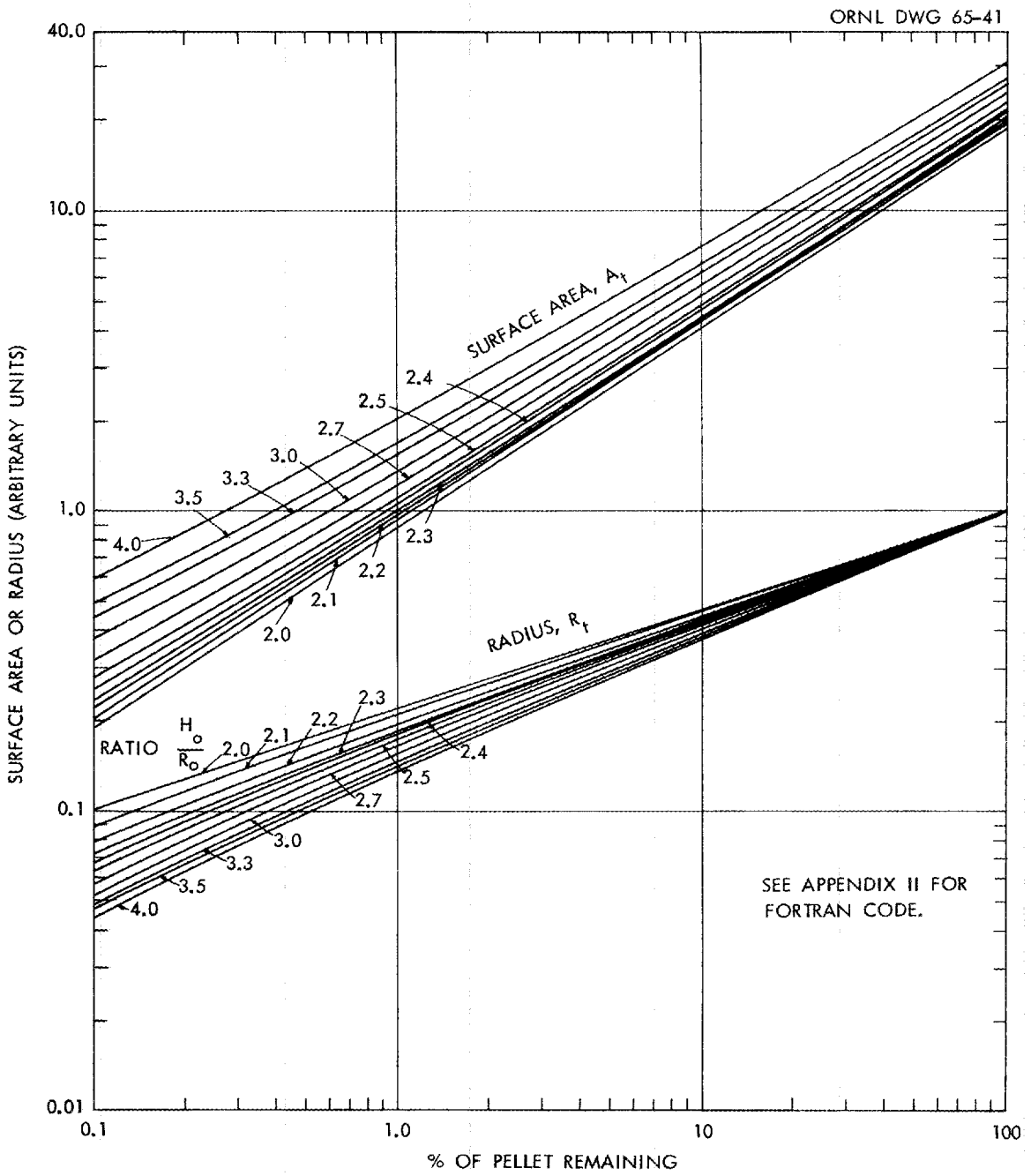


Fig. 20. Surface Area and Radius of Pellets While Dissolving: Effect of Ratio of Height to Radius. Initial radius = 1.

The increased surface area due to roughening decreased the time required for the pellets to dissolve. The roughening constant (RC) was defined as the integrated roughening factor and was calculated from the equation:

$$RC = \frac{\sum_{K=1}^{n} \frac{1}{(RF)_K} (R_{K-1} - R_K)}{R_o - R_n} , \qquad (17)$$

where R_o, R_K, and R_n are the radii at the initial, intermediate, and final times. The actual time (T) is then calculated by using this roughening constant and the theoretical dissolution time (t) [for instance from Eq. (15)]:

$$T = \frac{(RC)D_o\rho}{2(IDR)} . \qquad (18)$$

4.2 Total Dissolution of UO_2 Pellets

4.2.1 Effect of Excess Acid

A series of experiments with 6.9 to 33 moles of 6.2, 10.3, or 14.3 M HNO_3 per mole of uranium failed to show a difference in the times required to dissolve UO_2 pellets for various amounts of excess acid (Table A-14). However, the moles of acid consumed per mole of uranium dissolved varied with acidity and averaged 2.64, 2.82, and 3.36, respectively, for the three acidities. Since the solution was exposed to air during the reaction, the lower amount of acid consumption with the lower acidities may reflect only a greater efficiency of oxidation and recovery of nitrogen oxides in the condenser system during the longer time. A similar dependence was reported when dissolving uranium metal.[10]

4.2.2 Variation in Surface Area

In experiments with a large excess of acid, the roughness of the surface of the urania pellets increased to 3 to 5 times the initial roughness as the first half of the pellet dissolved, then remained fairly constant from about 50 to about 90% dissolution. When more then 90% had been dissolved, some of the pellets continued to dissolve rapidly,

while the final portions of others dissolved slowly. The time required to dissolve 90% was therefore reasonably reproducible, but the time required for complete solution could not be predicted.

The RC for dissolving about 90% of a group of UO_2 pellets in 6, 10, and 14 M HNO_3 was 0.42 ± 0.04 (Tables A-15, A-16, and A-17), with no significant variation with acid concentration (Fig. 21).

4.2.3 Variation with Source of Pellets

In spite of the wide variation in the IDR's for pellets of the same density but from different sources (see Sec 4.1.8), the total dissolution time for all pellets of similar composition and density was very nearly the same. The wide discrepancy in the IDR's between Davison I and Davison II pellets seems to be only a surface effect, and after a short time the dissolution rates of these pellets and pellets from other sources were about the same (Fig. 22, Tables A-18, A-19, A-20, and A-21). The average rates for dissolving pellets from Davison I, Atomics International, and United Nuclear in 14 M HNO_3 were 0.18, 0.14, and 0.17 mg cm^{-2} min^{-1}, respectively (Fig. 23). The maximum error in calculating the time for total dissolution (Eq. 15) using the average rate of 0.16 cm^{-2} min^{-1}, was only 15%.

4.3 Total Dissolution of PuO_2 Pellets

There was very little roughening of a PuO_2 pellet (density, 10.3 g/cm^3) as it dissolved in a 14 M HNO_3--0.05 M HF solution. About 9.5% of the pellet dissolved in the first 7.5 hr, and 85% dissolved in 86 hr (Fig. 24). Complete solution was not attempted because of the long time required. Heating was not continued overnight, but the pellet remained in the acid. As a result, the actual rate was even lower than indicated. The IDR, based on the calculated surface area of the pellet (Fig. 25), indicates that there was practically no increase in the roughness of the pellet as it dissolved (Table A-22). This is in marked contrast with the results observed when dissolving UO_2 pellets in nitric acid without fluoride (see Sec 4.2.2).

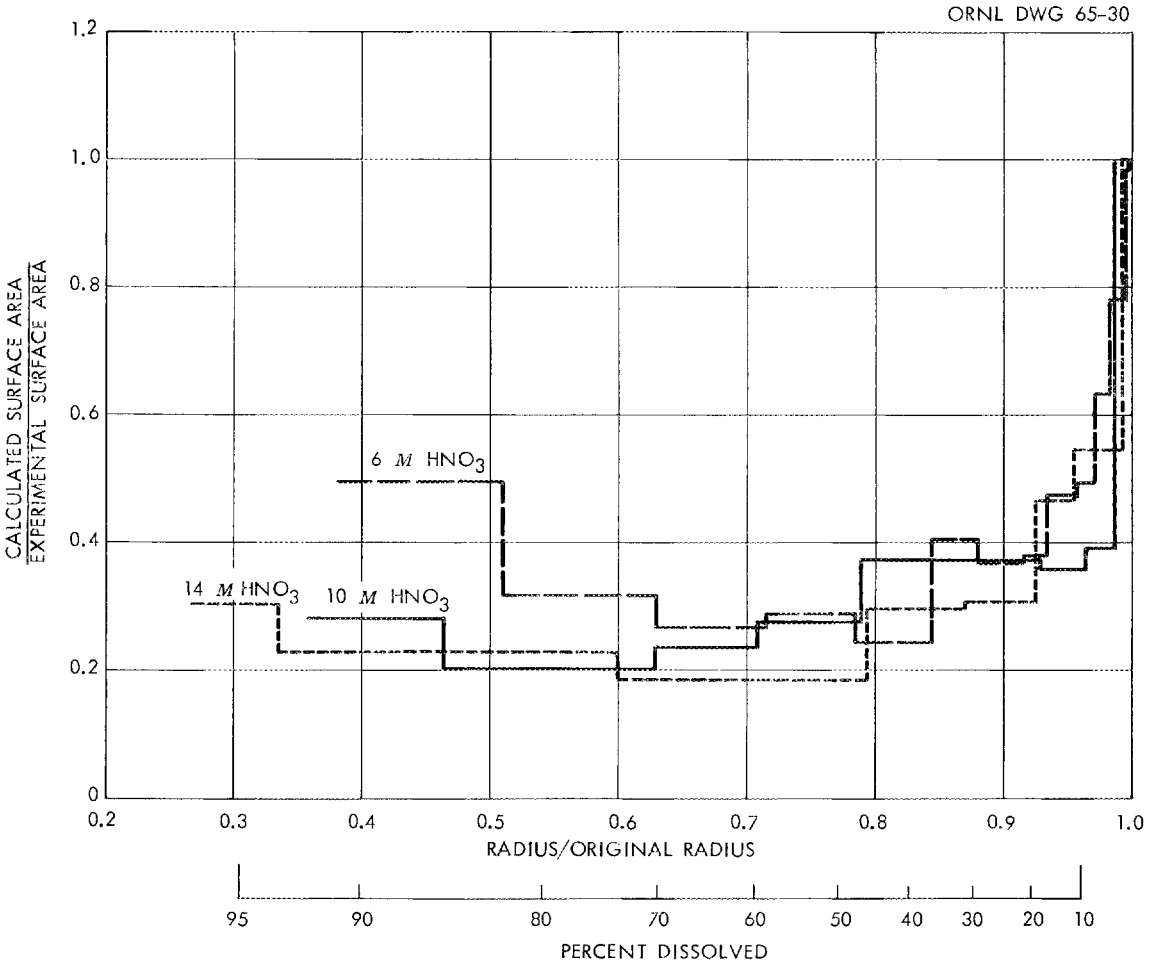


Fig. 21. Variation in Surface Roughness of UO_2 Pellets During Dissolving. (Dissolution time is proportional to the area under the curve.)

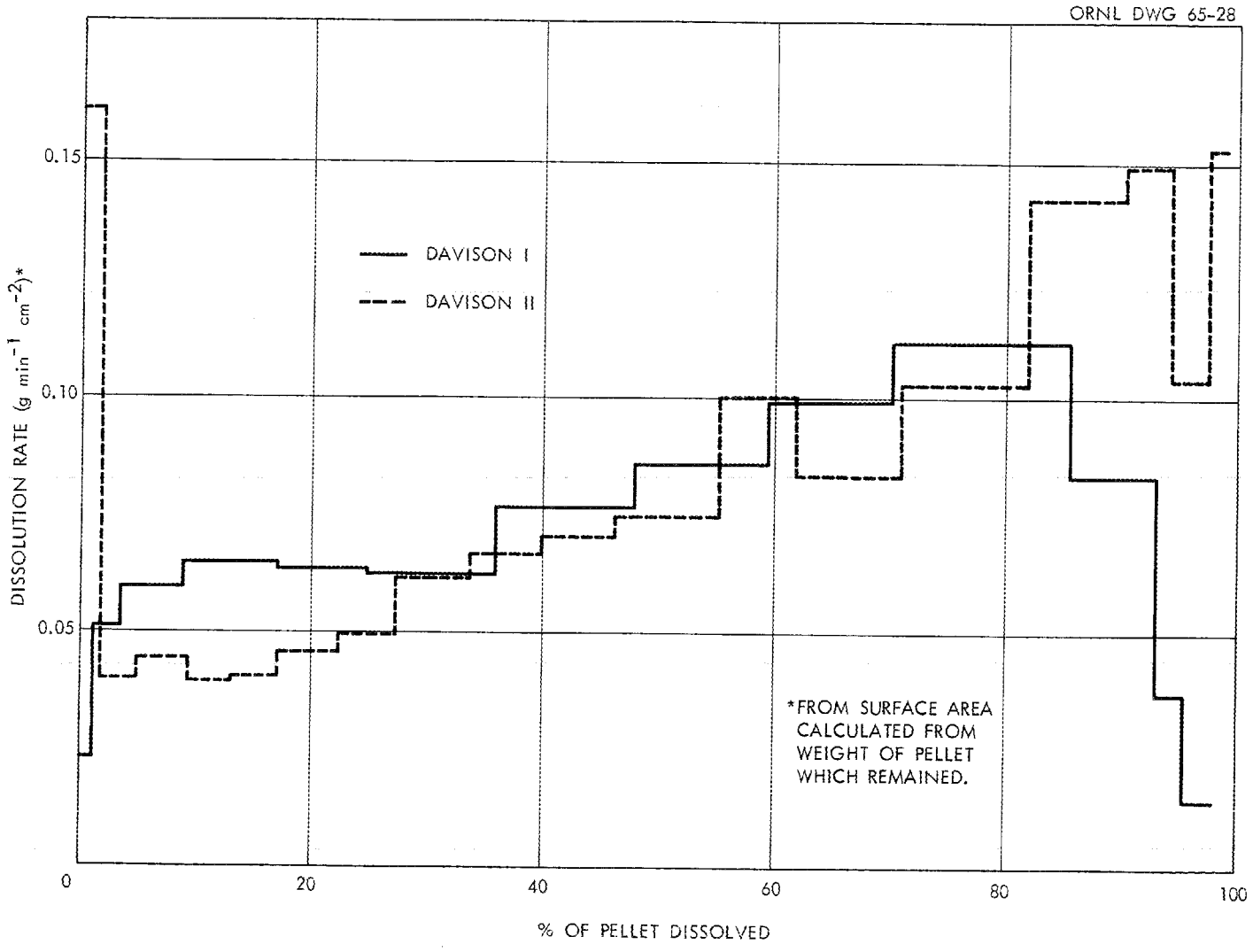


Fig. 22. Variation in the Dissolution Rates of Davison I and Davison II UO_2 Pellets While Dissolving. Density, 10.3 ± 0.1 g/cm^3 - 10 N HNO_3.

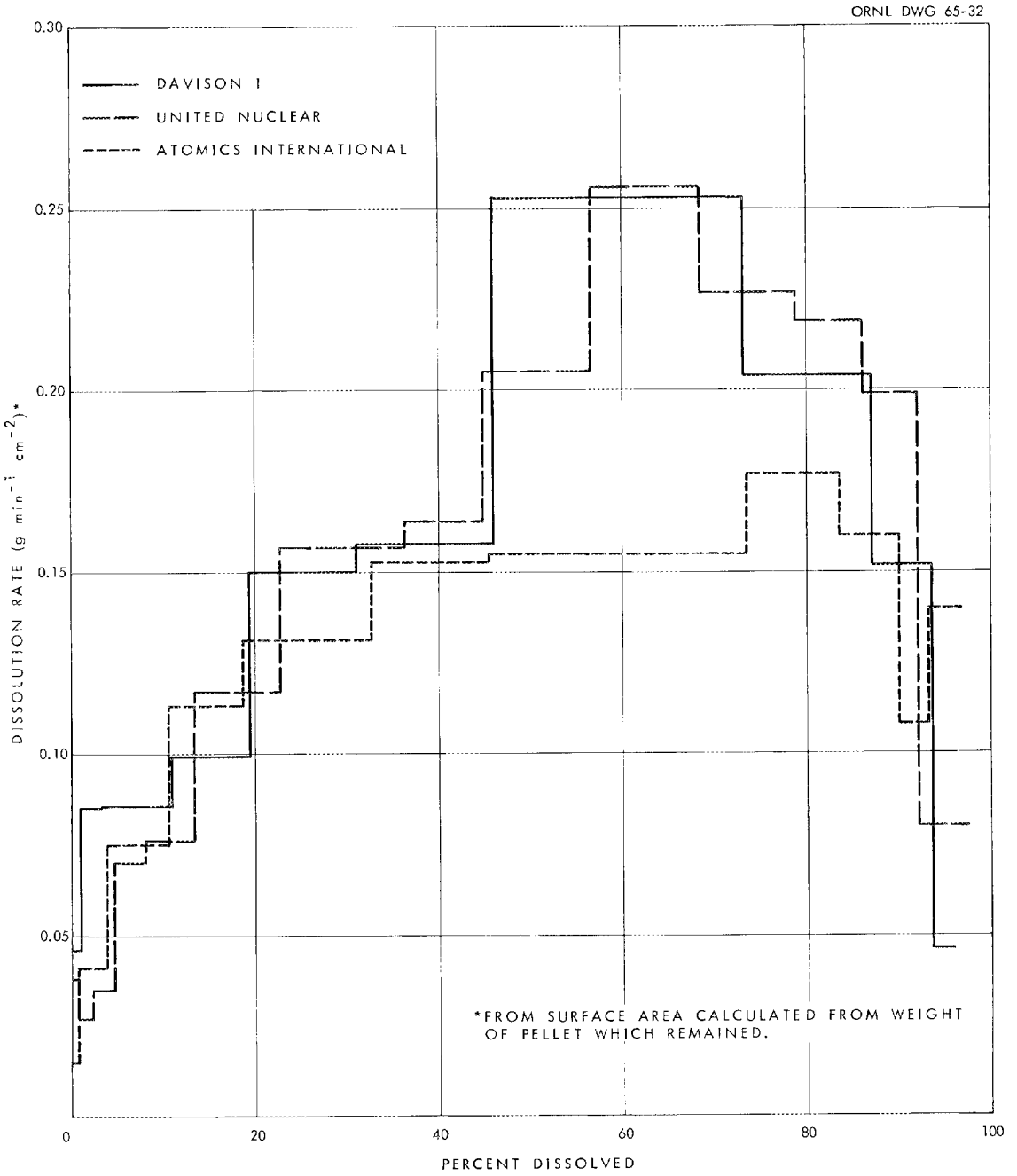


Fig. 23. Variation in the Dissolution Rates of UO_2 Pellets from Various Sources While Dissolving. Density, 10.3 g/cm^3 - 14 M HNO_3.

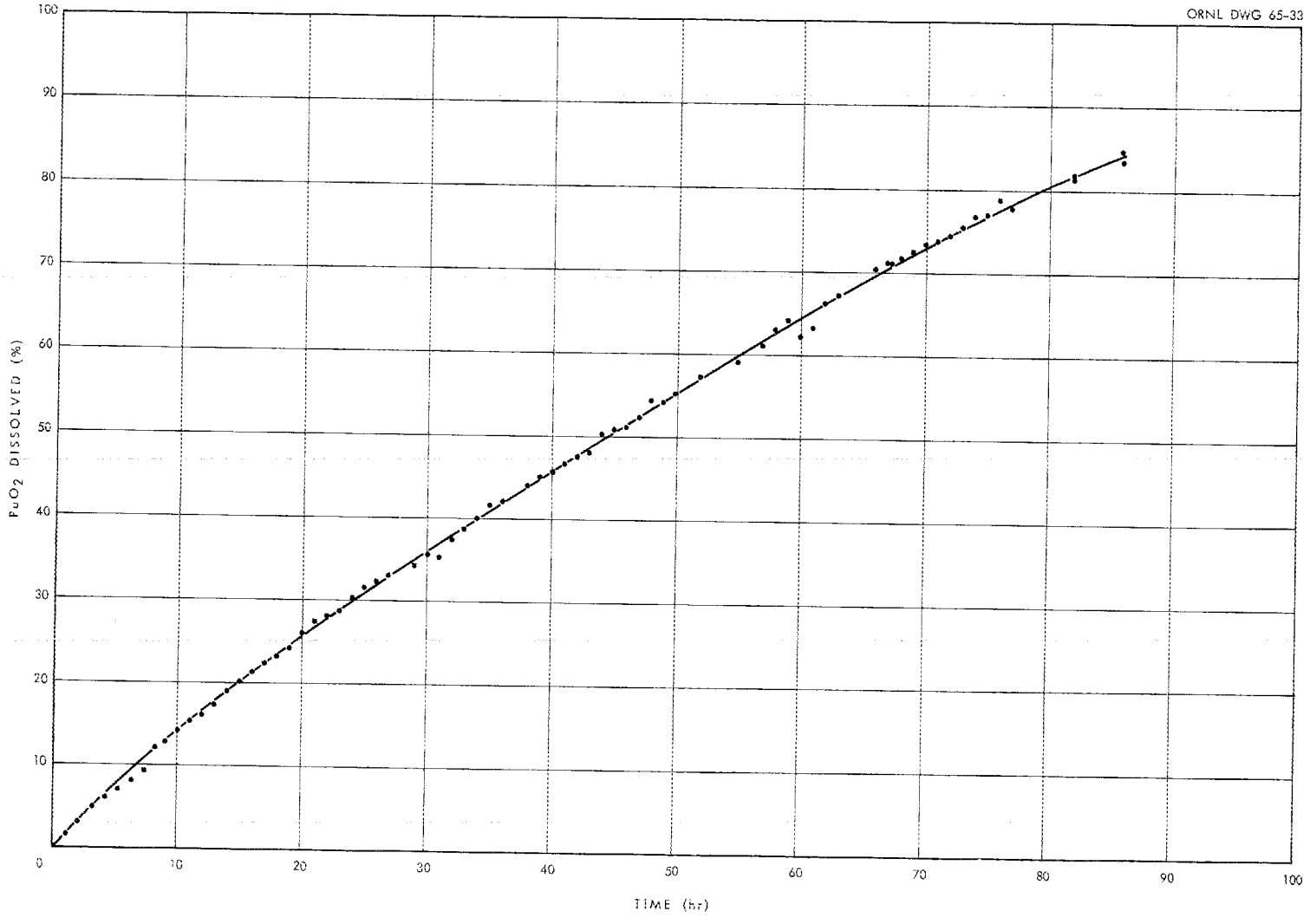


Fig. 24. Dissolution of a PuO_2 Pellet in 14 M HNO_3 - 0.05 M HF. Density = 10.3 g/cm^3.

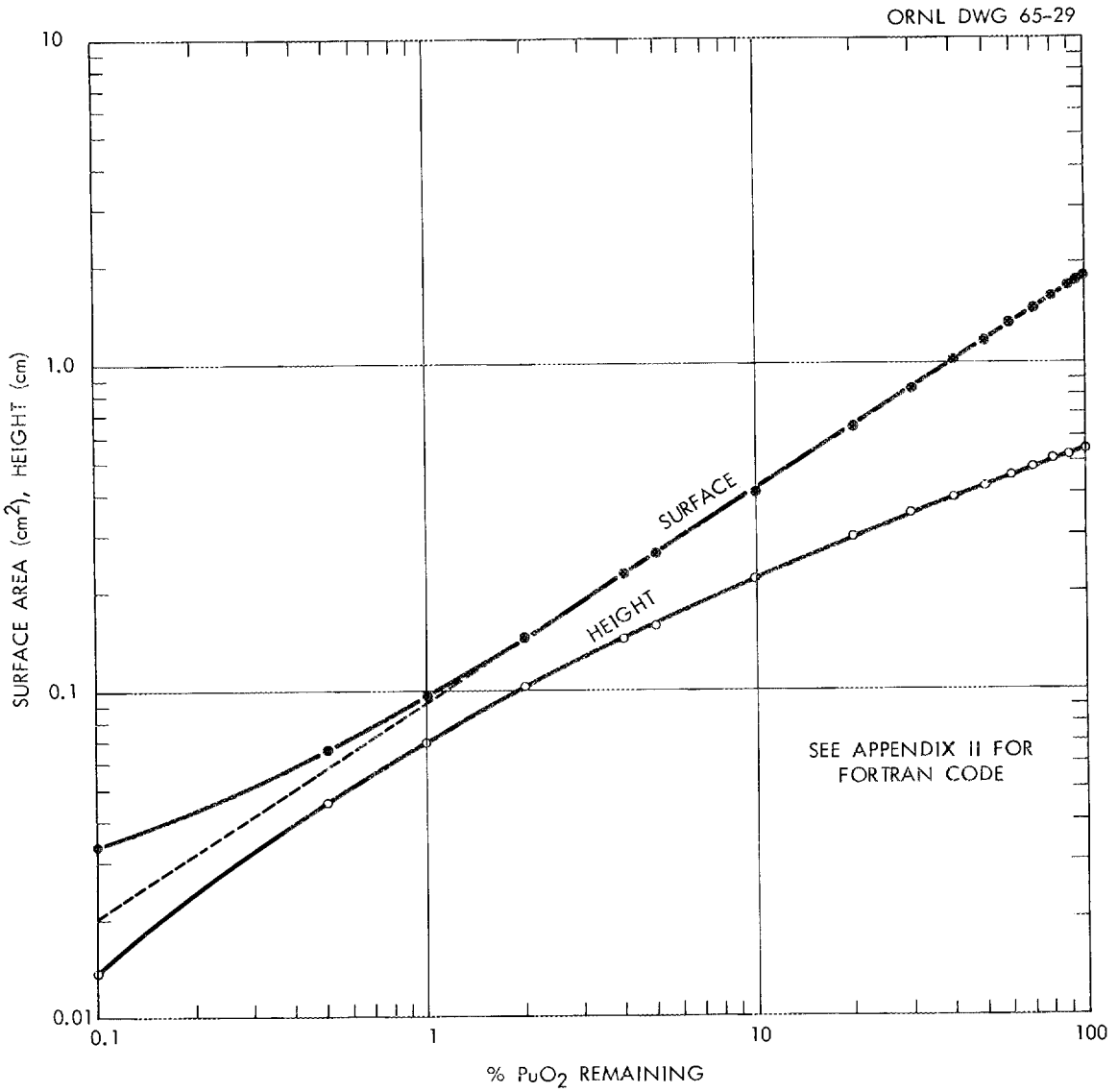


Fig. 25. Height and Surface Area of a NUMEC PuO_2 Pellet While Dissolving. (Assuming constant dissolution rate (mg min^{-1} cm^{-2}); initial height, 0.55 cm; initial radius = 0.335 cm.)

4.4 Total Dissolution of PuO_2-UO_2 Pellets

4.4.1 Effect of Fabrication Procedure

The time for dissolving PuO_2-UO_2 pellets and the IDR's (Sec 4.3.1) depend upon the method of fabrication of the pellets (Table 4). Only a limited variety of pellets was available for our experiments; however, some indication of the effect of the variables has been shown. Both mechanically blended and coprecipitated pellets containing less than 20% PuO_2 were completely dissolved in a 400% stoichiometric excess of 10 M HNO_3. The 20% PuO_2 pellets prepared from mechanically blended oxides sintered at 1600°C for 16 hr, and pellets prepared by coprecipitation and sintered at 1300°C for 2 hr were not completely dissolved in 10 M HNO_3 but were completely dissolved in 10 M HNO_3--0.05 M in HF. A similar mechanically blended 20% PuO_2-UO_2 pellet sintered for 48 hr at 1600°C, and 35% PuO_2 pellets prepared from coprecipitated materials sintered for 16 hr at 1600°C, were dissolved in 10 M HNO_3--0.05 M HF or in 14 M HNO_3 without fluoride (Fig. 26).

In the single case where a direct comparison can be made between pellets prepared by the two methods (5% PuO_2), the pellet prepared by coprecipitation dissolved slower than the pellets prepared from mechanically blended oxides (Fig. 27). With the 17.8% PuO_2 pellets, the variation in density obscures the comparison.

As had previously been shown in the rate studies (Sec 4.3.2), the increase in plutonium concentration increased the time for dissolution. Pellets prepared by coprecipitation and containing 0.5, 5.0, and 17.8% PuO_2 dissolved in 60, 240, and 360 min, respectively in 14 M HNO_3. In spite of the lower density (80% of theoretical), the pellet containing 17.8% PuO_2, prepared from mechanically blended powders, required 120 min to dissolve, whereas a similar pellet containing 5% PuO_2 (95% TD) dissolved in 80 min.

4.2.2 Preparation of Purex-Type Solvent Extraction Feed Solutions

The above total dissolution experiments were conducted using a large excess of nitric acid so that the acidity of the dissolvent would not

Table 4. Effect of Fabrication Procedure on Time Required for Total Dissolution of PuO_2-UO_2 Pellets

Plutonium Oxide-Uranium Oxide Sintered Pellets Prepared by Numec
Diameter: ~0.6 cm
Length: ~0.6 cm
400% Stoichiometric Excess of Nitric Acid

Pellet Composition % PuO_2	Oxide Preparation	Pelleting Pressure (tsi)	Sintering N_2-6% H_2 Temp. (°C)	Sintering N_2-6% H_2 Time (hr)	Percent Theoretical Density	Time for Total Dissolution in 10 M HNO_3 (min)
0.5	Coprecipitated[a]		1600	1	94	60
5.0	Mech. Blended[b]		1600	16	95	80
5.0	Coprecipitated	12.7	1600	1	95	240
17.8	Mech. Blended	13.4	1600	16	80	120
17.8	Coprecipitated	21.2	1600	16	93	360
20.0	Mech. Blended		1600	48	81	60
20.0	Mech. Blended	16.3	1600	16	93	60[c]
20.0	Coprecipitated	11.7	1300	2	87	30[d]
35.0	Coprecipitated	11.7	1600	16	88	450[e]

[a]Coprecipitated: $Pu(OH)_4$ and $(NH_4)U_3O_7$ continuously coprecipitated.

[b]Mech. Blended: Mechanically blended PuO_2 and UO_2.

[c]Only 91% of the plutonium dissolved.

[d]Only 79% of the plutonium dissolved.

[e]Only 85% of the plutonium dissolved.

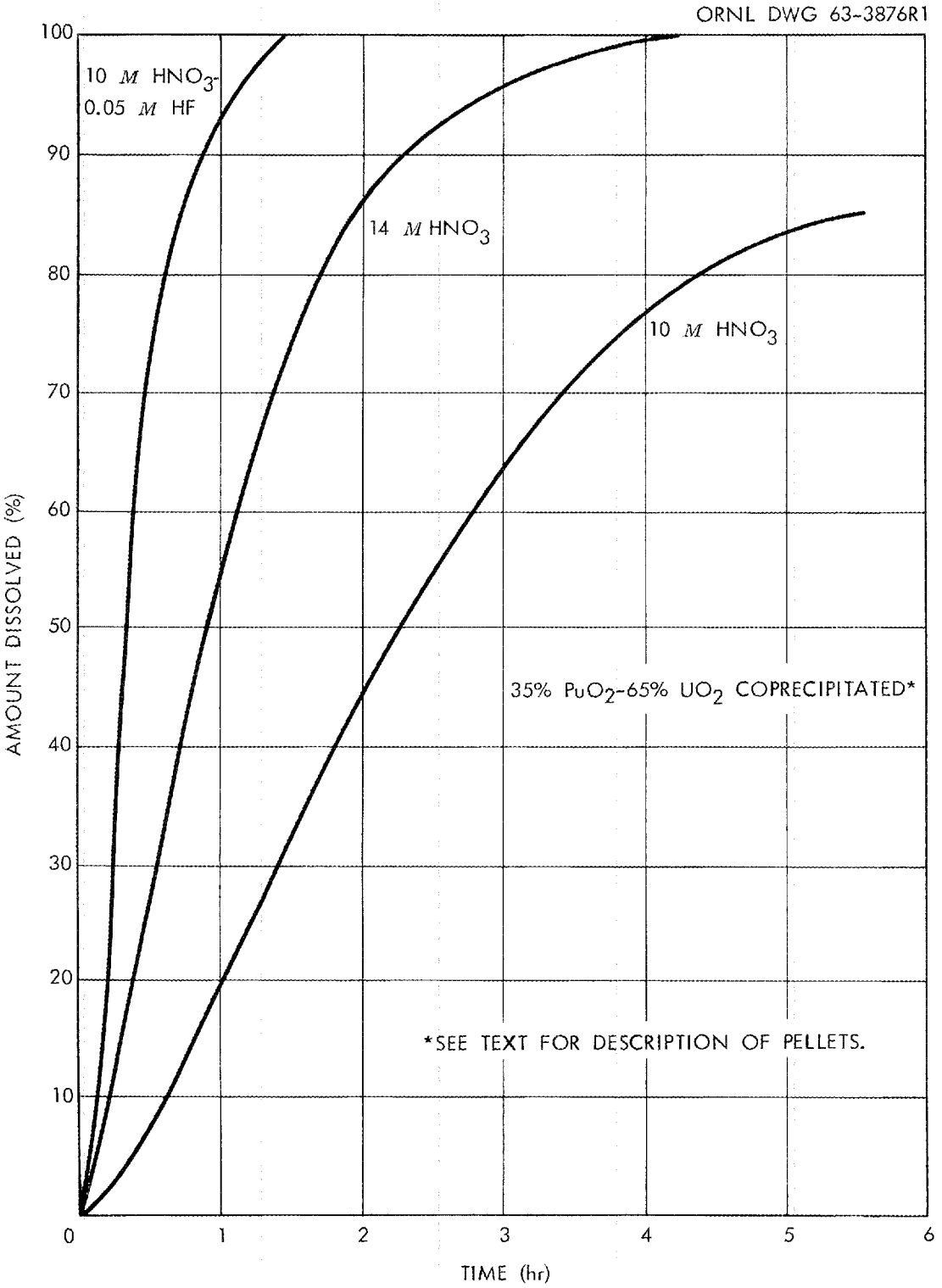


Fig. 26. Dissolution of 35% PuO_2-UO_2 in 10 M or 14 M HNO_3 or in 10 M HNO_3--0.05 M HF.

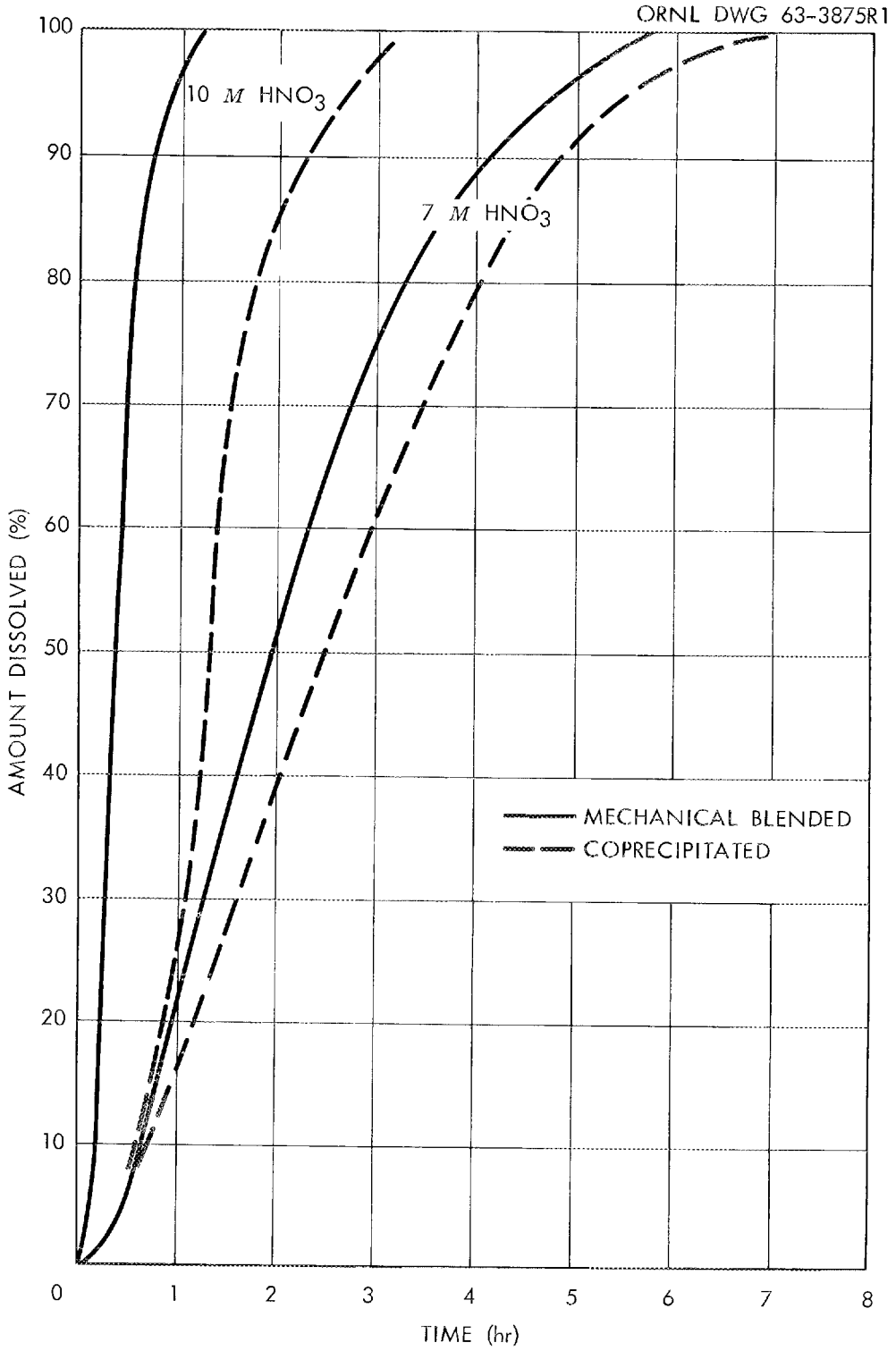


Fig. 27. Dissolution Rates of 5% PuO_2-UO_2 Pellets Prepared from Mechanical Blended or Coprecipitated Oxides.

vary widely as the samples dissolved. Processing could be simplified however if the fuel could be dissolved directly to produce a suitable Purex feed in a reasonable time and thereby eliminate the subsequent necessity of feed adjustment. For this study, a solution containing 1.5 moles of metal (uranium plus plutonium) in 3 M HNO_3 was assumed to be required for Purex feed. Several experiments (nitric acid without fluoride) resulted in at least 95% of the pellets dissolving in less than 24 hr. There was a small amount of residue from these experiments, and it remained undissolved when the solution was adjusted to 0.1 M HF and refluxed an additional 6 hr. The residue was presumed to be PuO_2, but there was not a sufficient quantity for analysis.

Feed-preparation experiments are continuing, but preliminary data indicate that a Purex feed solution may be prepared directly by dissolving nitric acid-soluble PuO_2-UO_2 pellets. Additional studies on a larger scale need to be made of the time required to dissolve pellets that have varying histories and compositions, of the effect of fluoride on dissolving pellets not completely soluble in nitric acid, and of the identification of the small residue.

4.4.3 Experiments Using Cyclic Dissolution Operations

A series of experiments were made in which multiple batches of 17 UO_2 pellets (150 g), were dissolved in 4.5, 6, or 10 M HNO_3. A batch of pellets was added to the boiling acid and dissolved for half the time required to dissolve completely. The solution was then removed, the residue washed, dried, and weighed. The residue together with a fresh batch of pellets was added to a fresh volume of boiling acid and the cycle repeated three times. After each cycle except the first, the dissolver solution contained about 200 g of uranium per liter. Although the sizes of the residual pieces varied considerably, there was little variation in total weight of residual "heel."

These experiments illustrate the effective use of a dissolver heel to shorten the cycle while preparing a reproducible dissolver solution.

The time required for dissolving a given fraction of charge was determined by taking intermediate samples while completely dissolving a

batch of pellets. For the three acidities, 4.5, 6.0, and 10 M HNO_3, the $t_{1/2}$ was 2.75, 1.5, and 0.5 hr, respectively — approximately inversely proportional to the square of the acidity. About 75% of the pellets dissolved in the half-time at any acidity.

The shape of the residual pellets after partially dissolving varied with the acidity. With 10 M HNO_3, the pellets were honeycombed, but had dissolved more or less uniformly from all surfaces. With 4.5 or 6 M HNO_3, the sides of the pellet dissolved faster than the ends; the pellets first became dumbell-shaped, and flat disks (the end surfaces of the cylinder) remainder after the rest of the pellet had dissolved. Due to the method of pressing, the ends of the pellets have the higher density, but no explanation has been found for the variation in attack with acidity.

A solution containing about 285 g U/l and 80 g Pu/l in about 3 M HNO_3 was prepared by dissolving 28% PuO_2-UO_2 pellets in 6.4 M HNO_3. These pellets were prepared by Vallecitos Atomic Laboratory by coprecipitation. They were 0.67 cm long, 0.55 cm diameter, and ranged from 91 to 94% of theoretical density. This solution was prepared by a cyclic dissolution in which about 70% of the pellets were dissolved in a 6 hr cycle. Assuming 6 M HNO_3, and an average density, the time for the cycle calculated using equations (7), (8), and (15) and Fig. 20 was 27 hr or 5 times the actual time required. Due to our assumptions, the time calculated for the cycle would have been too short instead of too long. This large variation between the calculated and experimental times is probably due to the differences in methods for pellet fabrication, which have not been adequately investigated in this program. The time required for the dissolution may be estimated by a single laboratory experiment involving the complete dissolution of a small group of pellets to determine the half time for the dissolution. By this method, the time for the cycle was predicted to within 30 min of the time required. Times for dissolution in other reagents or of similarly prepared pellets of other compositions could have similarly been accurately calculated.

4.4.4 Dissolution of Irradiated Pellets

The rate of dissolution in nitric acid of irradiated, swaged or pelletized 20% PuO_2--80% UO_2 were about a factor of five greater than those of unirradiated 20% PuO_2--80% UO_2 evaluated in this report. Dissolution of both the uranium and plutonium was essentially complete in 3 hr in 5 M HNO_3, but the uranium dissolved more rapidly than the plutonium during the first part of the dissolution.

The irradiated PuO_2-UO_2 used in these experiments was obtained from Vallecitos Atomic Laboratory.[12] The mixed oxide was prepared by co-precipitation and was either swaged into stainless steel tubes to ~75% of theoretical density or was pelletized to a density ~95% of theoretical and then loaded into stainless steel tubes. During irradiation, to burn-ups as high as 100,000 Mwd/metric ton, voids were formed in the centers of most specimens with an attendent increase in density of the oxide to 80 to 99% of the theoretical. After the irradiated tubes had been segmented and examined at Vallecitos, they were shipped to ORNL where they were used in dissolution experiments by J. H. Goode and co-workers.[13]

The initial rate of dissolution of 20% PuO_2-UO_2 in 10 M HNO_3 was estimated to be about 1 mg cm^{-2} min^{-1} from experiments using unirradiated PuO_2-UO_2 pellets (~93% of theoretical density) prepared by Nuclear Materials and Equipment Corporation. More recent experiments with unirradiated 28% PuO_2-UO_2 pellets prepared at Vallecitos indicated a dissolution rate of ~3 mg cm^{-2} min^{-1} in 6 M HNO_3. The rate of dissolution of the irradiated 20% PuO_2--80% UO_2 was so much faster than estimated that the sampling schedule during the first several experiments did not result in enough analyses to allow calculation of the initial dissolution rate. Four subsequent experiments were conducted, three with 5 M HNO_3 and one with 3 M HNO_3, all without fluoride, in which an estimate of the initial rate of dissolution of the irradiated oxides was obtained. In two experiments the stainless steel clad was dissolved in sulfuric acid. In the other two experiments the oxide was leached from the clad.

There was considerable scatter in the data, but in each experiment using 5 M HNO_3 the first samples of the solution contained a ratio U/Pu

of about 10, whereas the mixed oxide was calculated to contain a ratio of about 6.6 after irradiation. At the end of the dissolution the ratio of the solution was between 5 and 6.6. The small residue at the end of the dissolution did not contain a significant portion of the plutonium or uranium. The rate of dissolution of the irradiated oxide was greater than that obtained with unirradiated PuO_2-UO_2. The experiment that gave the most easily interpretable results consisted of the decladding then the dissolution in 5 M HNO_3 of two PuO_2-UO_2 pellets and one UO_2 pellet (V-3-P)* which had been irradiated to 54,400 Mwd/metric ton. The UO_2 pellet was dissolved in a separate experiment and therefore acted as a control. All three pellets dissolved at a rate of about 25 mg cm^{-2} min^{-1}. If the pellets were of the same percent of theoretical density, these results are in marked contrast to those obtained earlier[3] where pellets containing PuO_2 dissolved much more slowly than UO_2 pellets. In the previous experiments, unirradiated UO_2 pellets (93% of theoretical density) dissolved at a rate of about 10 mg cm^{-2} min^{-1} in boiling 4.5 M HNO_3.

The other three experiments consisted of the dissolution of swaged oxides. In one experiment (IV-4-S),* the oxide was declad then dissolved in 5 M HNO_3. The declad oxide cylinder had a void through the center and consisted of 3 large and several small pieces and some powder. Assuming that the surface area was the same as that of three right cylinders having a total length of the original swaged oxide, the dissolution rate would have been ~8 mg cm^{-2} min^{-1}. The third experiment (V-1-S)* consisted of leaching swaged oxide from two segments of tubing with 5 M HNO_3. The surface of the void was very irregular as shown in a photograph; therefore, the rate of dissolution per unit of area could not be determined. The oxide dissolved at a rate of 28 mg/min, which was very fast considering the surface exposed after sectioning the capsule. This rate corresponds to a dissolution rate of 7 mg cm^{-2} min^{-1} based on exposure of both inside and outside surfaces of the oxide if the surfaces were smooth. In a similar experiment using 3.5 M HNO_3 (VIII-1-S)*, the oxide dissolved at rates of 35 mg/min, or 6 mg cm^{-2} min^{-1} on a similar basis.

---

*Refer to experiment numbers in reference 13.

The data from these experiments are not adequate for dissolution-rate determinations, but the experiments demonstrated rapid and essentially complete dissolution of irradiated PuO_2-UO_2 in dilute nitric acid without fluoride and under conditions similar to those expected in a fuel processing plant.

4.4.5 Recommendations for a Commercial Facility

The data in this report indicate that the best dissolvent for PuO_2-UO_2 pellets in a commercial processing facility would be a mixture of nitric and hydrofluoric acids.

Some PuO_2-UO_2 pellets containing as much as 35% PuO_2 could be completely dissolved in nitric acid alone; however, with other pellets under similar conditions, a plutonium-rich residue remained in the dissolver, and it dissolved very slowly in nitric acid. Such a residue would be hazardous in a commercial operation since it may be difficult to detect and might accumulate in the dissolver vessel or waste tanks. This residue seems to be associated with lower temperature and shorter times in the firing of the pellets and is more likely to occur as the concentration of plutonium in the pellet increases or when the pellets are made with mechanically blended oxides rather than with coprecipitated materials. Fabrication conditions could quite likely be found which would ensure that the pellets are completely soluble in nitric acid, but such pellets are not required for the reactor. The cost of a dissolver designed to accommodate the nitric acid-hydrofluoric acid mixture would probably be more economical than ensuring that all pellets are in solid solution.

5. REFERENCES

1. L. M. Ferris and A. H. Kibbey, Sulfex-Thorex and Darex-Thorex Processes for the Dissolution of Consolidated Edison Power Reactor Fuel: Laboratory Development, ORNL-2934 (October 1960).

2. C. D. Watson, B. C. Finney, G. A. West, and B. A. Hannaford, The Shear-Leach Process for Spent Nuclear Fuels, ORNL-3625 (in press).

3. R. F. Taylor, E. W. Sharratt, L. E. M. de Chazel, and D. H. Logsdail, "Dissolution Rates of Uranium Dioxide Sintered Pellets in Nitric Acid Systems," J. Applied Chem. 13, pp 32-40 (January 1963).

4. H. F. Johnson, Analysis of UO_2 Dissolution in Nitric Acid Solution, ORNL-3297 (September 4, 1962) also p 49 in ORNL-CF-61-3-67.

5. Plutonium Used as a Fuel in Nuclear Reactors, EURAEC-80, Belgonucleaire, United States-Euratom Joint Research and Development Program Quarterly Report No. 3, January-March 1961.

6. J. K. Davidson, W. O. Haas, Jr., J. L. Meroherter, R. S. Miller, and D. J. Smith, The Fast Oxide Breeder: The Fuel Cycle, KAPL-1757 (July 1959).

7. W. D. Bond, Dissolution of Sintered Thorium-Uranium Oxide Fuels in Nitric Acid, ORNL-2519 (Oct. 28, 1958).

8. Progress Report: Development of Plutonium-Bearing Fuel Materials, NUMEC-100 through 105 (March 1962-June 1963).

9. J. F. Flagg, Chemical Processing of Reactor Fuels, Academic Press, N.Y., 1961, p 90.

10. R. E. Blanco and C. D. Watson, "Headend Processes for Solid Fuels," Reactor Handbook, Vol II, Fuel Reprocessing, Interscience Publishers, N.Y., 1961, p 60.

11. A. S. Wilson, "Method of Dissolving Plutonium Dioxide in Nitric Acid Using Cerium Ions," U.S. Patent 3,005,682 (Oct. 24, 1961).

12. J. M. Gerhart, Post Irradiation Examination of a PuO_2-UO_2 Fast Reactor Fuel, GEAP-3833 (November 1961).

13. J. H. Goode, Hot Cell Dissolution of Highly Irradiated 80% UO_2--20% PuO_2 Fast Reactor Fuel Specimens, ORNL-3754 (in preparation).

6. APPENDIX I

6.1 Tables of Data

The tables which are necessary to substantiate the conclusions of this report but which are not required for the understanding of the narration have been included as an appendix.

Table A-1. Dissolution Rates of UO_2 Pellets in Nitric Acid

Pellet Density: 10.3 ± 0.1 g/cm^3

HNO_3 Conc. (M)	Boiling Point (°C)	Instantaneous Dissolution Rate mg UO_2 cm^{-2} min^{-1}		% Pellet Dissolved	
		Physical	Chemical	Physical	Chemical
2.0	100.5	0.81	0.80	0.8	0.8
2.0	100.5	1.08	1.04	1.1	1.0
2.0	102.0	0.88	0.87	0.9	0.8
2.0	102.0	0.84	0.82	0.8	0.8
4.0	104.0	3.70	3.50	0.9	0.9
4.0	104.0	4.23	3.67	1.0	0.9
4.0	104.0	4.29	3.84	1.0	0.9
6.0	106.5	9.96	9.07	2.4	2.2
6.0	106.0	11.41	10.18	2.8	2.5
6.0	106.0	9.79	8.82	2.4	2.1
8.0	110.5	16.89	15.56	2.5	2.3
8.0	110.0	12.92	11.42	1.3	1.1
8.0	110.0	15.14	13.31	2.2	2.0
10.0	---	23.57	22.22	2.3	2.2
10.0	113.5	34.46	31.07	2.6	2.3
10.0	113.5	25.09	22.82	1.8	1.7
12.0	118.0	49.00	44.15	2.4	2.2
12.0	117.5	47.09	42.36	2.3	2.1
12.0	118.0	38.20	33.06	1.8	1.6
14.0	119.0	59.36	45.95	1.5	1.1
14.0	119.0	49.56	41.35	1.2	1.0
14.0	119.0	62.11	45.30	1.5	1.1
15.6	118.5	70.29	58.39	1.7	1.4
15.6	118.5	49.70	41.37	1.2	1.0
15.6	120.0	64.81	50.95	1.6	1.2

Table A-2. Dissolution Rates of UO_2 Pellets in Nitric Acid-Hydrofluoric Acid

Pellet Density: 10.3 ± 0.1 g/cm^3

Concentration (M)		Instantaneous Dissolution Rate mg UO_2 cm^{-2} min^{-1}	
HNO_3	HF	Physical	Chemical
2.0	0.005	0.53	0.52
2.0	0.005	0.46	0.44
2.0	0.005	0.45	0.44
6.0	0.005	5.52	5.57
6.0	0.005	6.13	5.96
6.0	0.005	6.00	5.91
10.0	0.005	17.96	16.12
10.0	0.005	23.99	23.06
10.0	0.005	17.19	16.33
14.0	0.005	46.09	41.26
14.0	0.005	36.06	32.37
14.0	0.005	43.32	34.55
2.0	0.01	0.43	0.41
2.0	0.01	0.64	0.63
2.0	0.01	0.61	0.58
6.0	0.01	5.70	5.36
6.0	0.01	6.33	5.76
6.0	0.01	6.40	5.92
10.0	0.01	15.74	14.40
10.0	0.01	16.43	14.14
10.0	0.01	19.33	19.76
14.0	0.01	31.66	27.09
14.0	0.01	38.67	33.80
14.0	0.01	40.38	36.92
2.0	0.05	1.02	1.02
2.0	0.05	1.53	1.46
2.0	0.05	1.30	1.26
2.0	0.05	1.08	1.17
2.0	0.05	1.16	1.20
3.0	0.05	2.37	2.53
3.0	0.05	2.66	2.65
3.0	0.05	2.48	2.54
6.0	0.05	7.65	7.22
6.0	0.05	4.48	4.42
6.0	0.05	4.36	4.05
6.0	0.05	4.57	5.39
6.0	0.05	4.74	5.81
10.0	0.05	12.94	11.22
10.0	0.05	13.22	11.80
10.0	0.05	12.06	9.93
14.0	0.05	27.35	25.47
14.0	0.05	28.37	25.54
14.0	0.05	28.22	25.39
14.0	0.05	23.23	20.40
14.0	0.05	24.04	22.06
14.0	0.05	25.72	23.88
14.0	0.05	25.02	22.74
14.0	0.05	25.03	22.91
2.0	0.1	1.86	1.79
2.0	0.1	2.10	2.10
2.0	0.1	1.84	1.90
6.0	0.1	5.49	5.52
6.0	0.1	6.49	6.35
6.0	0.1	6.90	7.13
10.0	0.1	10.22	9.79
10.0	0.1	13.63	13.06
10.0	0.1	12.15	10.87
14.0	0.1	25.74	20.48
14.0	0.1	20.97	15.73
14.0	0.1	22.84	20.71
2.0	0.5	0.81	0.87
2.0	0.5	0.87	0.84
6.0	0.5	4.63	4.57
6.0	0.5	3.77	3.73
10.0	0.5	12.51	11.56
10.0	0.5	12.07	11.42
14.0	0.5	30.45	27.77
14.0	0.5	32.16	28.03
2.0	1.5	1.29	1.40
2.0	1.5	0.85	0.76
6.0	1.5	7.11	8.10
6.0	1.5	6.66	6.80
6.0	1.5	5.99	5.99
10.0	1.5	14.05	13.73
10.0	1.5	10.03	9.32

Table A-3. Dissolution Rates of UO_2 Pellets in Nitric Acid Containing Hydrofluoric Acid and Aluminum Nitrate

Pellet Density: 10.3 ± 0.1 g/cm^3
Al/F mole ratio = 3

Concentration (M)			Boiling Point (°C)	Instantaneous Dissolution Rate (mg UO_2 cm^{-2} min^{-1})	
HNO_3	HF	Al		Physical	Chemical
2.0	0.005	0.015	102.0	1.25	1.18
2.0	0.005	0.015	102.0	0.77	0.74
2.0	0.005	0.015	102.0	0.95	0.93
6.0	0.005	0.015	108.0	10.39	9.97
6.0	0.005	0.015	108.0	6.81	6.43
6.0	0.005	0.015	108.0	9.05	8.25
10.0	0.005	0.015	115.0	29.05	27.26
10.0	0.005	0.015	114.5	25.08	22.79
10.0	0.005	0.015	114.5	26.97	23.84
14.0	0.005	0.015	118.0	58.21	49.94
14.0	0.005	0.015	118.0	70.02	56.93
14.0	0.005	0.015	118.0	56.56	51.13
2.0	0.01	0.03	102.0	1.05	0.97
2.0	0.01	0.03	102.0	1.23	1.17
2.0	0.01	0.03	102.0	1.42	1.36
6.0	0.01	0.03	108.0	10.54	9.93
6.0	0.01	0.03	108.0	8.51	7.94
6.0	0.01	0.03	108.0	11.62	10.75
10.0	0.01	0.03	114.0	34.80	31.24
10.0	0.01	0.03	114.0	27.30	24.89
10.0	0.01	0.03	114.6	19.97	17.84
14.0	0.01	0.03	119.0	68.89	58.44
14.0	0.01	0.03	119.0	56.74	47.95
14.0	0.01	0.03	119.0	57.16	48.91
2.0	0.05	0.15	102.0	1.46	1.43
2.0	0.05	0.15	102.0	1.03	1.08
2.0	0.05	0.15	102.0	1.28	1.24
6.0	0.05	0.15	108.5	9.08	8.98
6.0	0.05	0.15	108.5	9.50	9.36
6.0	0.05	0.15	109.0	13.09	12.87
10.0	0.05	0.15	115.0	24.93	23.36
10.0	0.05	0.15	115.0	25.70	23.85
10.0	0.05	0.15	115.0	23.11	21.55
14.0	0.05	0.15	118.0	72.12	65.02
14.0	0.05	0.15	118.0	88.59	80.92
14.0	0.05	0.15	118.5	60.74	53.36
2.0	0.1	0.3	102.5	1.85	1.84
2.0	0.1	0.3	102.5	1.57	1.56
2.0	0.1	0.3	102.5	1.60	1.59

Table A-3. Dissolution Rates of UO_2 Pellets in Nitric Acid Containing Hydrofluoric Acid and Aluminum Nitrate

(Continued)

Concentration (M)			Boiling Point (°C)	Instantaneous Dissolution Rate ($mg\ UO_2\ cm^{-2}\ min^{-1}$)	
HNO_3	HF	Al		Physical	Chemical
6.0	0.1	0.3	109.0	12.33	12.05
6.0	0.1	0.3	109.0	15.28	15.00
6.0	0.1	0.3	109.5	9.92	9.74
10.0	0.1	0.3	116.0	24.99	24.13
10.0	0.1	0.3	116.0	34.26	33.26
10.0	0.1	0.3	116.0	35.53	33.61
14.0	0.1	0.3	118.5	73.12	71.13
14.0	0.1	0.3	---	73.95	67.99
14.0	0.1	0.3	---	63.23	55.60

Table A-4. Dissolution Rates of UO_2 Pellets in Nitric Acid Containing 0.3 M $Al(NO_3)_3$

Pellet Density: $10.3 \pm 0.1\ g/cm^3$

HNO_3 Conc. (M)	Boiling Point (°C)	Instantaneous Dissolution Rate ($mg\ UO_2\ cm^{-2}\ min^{-1}$)	
		Physical	Chemical
2.0	102.5	2.02	1.87
2.0	102.5	1.89	1.77
6.0	109.0	14.38	13.81
6.0	109.5	8.75	8.05
10.0	116.0	36.60	35.60
10.0	116.0	26.09	24.25
10.0	116.0	44.68	39.99
13.3	119.5	60.80	50.14
13.3	119.5	59.46	52.35
13.3	120.0	46.48	44.77

Table A-5. Dissolution Rates of UO_2 Pellets in Nitric Acid Containing Sodium or Lithium Nitrate

Pellet Density: 10.3 ± 0.1 g/cm^3

Concentration (M)			Boiling Point (°C)	Instantaneous Dissolution Rate (mg UO_2 cm^{-2} min^{-1})	
HNO_3	$NaNO_3$	$LiNO_3$		Physical	Chemical
2.0	1.0	---	103.0	1.86	1.81
2.0	1.0	---	103.0	2.27	2.16
2.0	1.0	---	103.0	1.61	1.52
6.0	1.0	---	108.5	12.31	12.03
6.0	1.0	---	108.5	14.55	14.97
6.0	1.0	---	109.0	11.40	10.97
10.0	1.0	---	116.0	21.10	20.53
10.0	1.0	---	116.0	30.69	29.83
10.0	1.0	---	116.0	29.18	26.90
13.0	---	1.0	119.5	55.47	49.78
13.0	---	1.0	119.5	52.65	47.21
13.0	---	1.0	119.5	36.84	34.58
2.0	2.0	---	104.0	2.63	2.63
2.0	2.0	---	104.0	2.61	2.61
2.0	2.0	---	104.0	2.89	2.70
2.0	2.0	---	104.0	2.73	2.56
2.0	---	2.0	105.0	2.77	2.80
6.0	2.0	---	111.0	16.08	15.29
6.0	2.0	---	111.0	16.53	16.53
6.0	---	2.0	112.0	14.75	14.16
6.0	---	2.0	112.0	14.16	13.60
10.0	---	2.0	118.0	43.55	42.14
10.0	---	2.0	118.0	51.25	49.12
10.0	---	2.0	118.0	55.86	54.43
13.0	---	2.0	120.0	69.99	63.97
13.0	---	2.0	121.0	68.01	63.20
13.0	---	2.0	120.0	72.85	69.14
2.0	---	4.0	109.0	9.68	6.92
2.0	---	4.0	109.0	7.92	7.97
2.0	---	4.0	109.0	7.59	7.54
2.0	---	8.0	119.0	39.19	38.34
2.0	---	8.0	119.0	38.20	37.49
2.0	---	8.0	119.0	40.18	39.90

Table A-6. Dissolution Rates of UO_2 Pellets in Nitric Acid Containing Uranyl Nitrate

Pellet Density: 10.3 ± 0.1 g/cm^3

HNO_3 Conc. (M)	$UO_2(NO_3)_2$ Conc. (M)	Boiling Point (°C)	Instantaneous Dissolution Rate (mg UO_2 cm^{-2} min^{-1}) Physical
2.0	0.5	101.0	1.40
2.0	0.5	102.0	1.40
2.0	0.5	101.0	1.74
3.4	0.5	105.0	3.85
3.4	0.5	105.0	3.79
3.4	0.5	105.0	2.71
6.0	0.5	109.0	14.63
6.0	0.5	109.0	6.77
6.0	0.5	109.0	9.84
12.0	0.5	118.0	31.86
12.0	0.5	118.0	33.48
12.0	0.5	118.0	44.66
2.0	1.5	106.0	3.65
2.0	1.5	106.0	4.37
2.0	1.5	106.0	3.37
4.0	1.5	109.0	7.99
4.0	1.5	109.0	9.20
4.0	1.5	109.0	6.90
7.0	1.5	114.0	19.57
7.0	1.5	115.0	19.34
7.0	1.5	114.0	13.85
12.0	1.5	121.0	64.78
12.0	1.5	121.0	62.27
12.0	1.5	121.0	87.67

Table A-7. Dissolution Rates of UO_2 Pellets in Nitric Acid Containing Sodium Nitrite

Pellet Density: 10.3 ± 0.1 g/cm^3

HNO_3 Conc. (M)	$NaNO_2$ Conc. (M)	Boiling Point (°C)	Instantaneous Dissolution Rate (mg UO_2 cm^{-2} min^{-1})	
			Physical	Chemical
2.0	0.02	102.0	0.98	0.93
2.0	0.02	102.5	1.04	1.00
2.0	0.02	102.0	0.78	0.74
6.0	0.02	108.0	9.09	9.75
6.0	0.02	108.0	9.40	9.51
6.0	0.02	108.0	10.47	10.38
10.0	0.02	114.5	18.13	17.56
10.0	0.02	114.0	21.46	20.18
10.0	0.02	114.0	21.90	23.03
14.0	0.02	119.0	45.35	43.09
14.0	0.02	119.0	71.93	62.46
14.0	0.02	119.0	52.11	50.69
2.0	0.2	102.0	1.14	1.13
2.0	0.2	102.0	0.93	0.94
2.0	0.2	102.0	0.82	0.82
6.0	0.2	107.5	6.76	6.71
6.0	0.2	107.5	7.64	7.26
6.0	0.2	108.0	8.38	7.86
10.0	0.2	114.0	18.16	18.02
10.0	0.2	114.0	19.13	25.93
10.0	0.2	114.0	22.22	23.07
14.0	0.2	119.0	55.94	
14.0	0.2	119.0	50.26	44.33
14.0	0.2	119.0	80.35	73.80

Table A-8. Dissolution Rates of UO_2 Pellets: Variation with Fabricator and Density

Fabricator	Pellet Density, (% of Theo.)	Bulk Density (g/cm^3)	HNO_3 Conc. (M)	Instantaneous Dissolution Rate ($mg\ UO_2\ cm^{-2}\ min^{-1}$) Physical	Chemical	O/U Ratio in Pellet
NUMEC	94.6	10.41	6.0	1.64	3.42	2.001
NUMEC	95.8	10.54	6.0	1.38	1.26	2.001
NUMEC	96.2	10.58	6.0	2.77	2.77	2.001
Davison (I)	93.6±0.9	10.3±0.1	6.0	9.70	9.27	2.001
Davison (I)	93.6±0.9	10.3±0.1	6.0	9.96	9.07	2.001
Davison (I)	93.6±0.9	10.3±0.1	6.0	11.41	10.18	2.001
Davison (I)	93.6±0.9	10.3±0.1	6.0	9.79	8.82	2.001
Davison (II)	93.6	10.30	6.0	54.53	50.1	2.006
Davison (II)	94.3	10.37	6.0	48.60	46.2	2.006
United Nuclear	93.6	10.30	6.0	2.68	3.76	2.002
United Nuclear	93.6	10.30	6.0	5.89	6.09	2.002
United Nuclear	93.6	10.30	6.0	6.64	6.44	2.002
United Nuclear	93.6	10.31	6.0	4.13	4.20	2.002
Atomics Int'l.	94.0	10.34	6.0	2.93	2.81	2.001
Atomics Int'l.	93.8	10.32	6.0	1.89	2.02	2.001
Westinghouse	93.0	10.23	6.0	1.21	1.00	2.001
Westinghouse	93.1	10.24	6.0	1.37	1.31	2.001
Westinghouse	94.3	10.37	6.0	0.76	0.66	2.001
ORNL	94.0	10.34	6.0	7.02	6.67	2.1244
ORNL	91.1	10.02	6.0	0.72	0.70	2.0555
ORNL	93.0	10.23	6.0	0.26	0.31	---
ORNL	85.0	9.35	6.0	14.99	13.9	2.0237
ORNL	83.8	9.22	6.0	10.59	11.8	2.0400
ORNL	83.7	9.21	6.0	10.64	10.4	2.0400
ORNL	71.8	7.90	6.0	36.22	25.1	2.0900
ORNL	68.7	7.56	6.0	46.29	---	---
ORNL	70.2	7.72	6.0	31.60	36.4	---
ORNL	86.7	9.54	6.0	4.73	4.40	---
ORNL	91.8	10.10	6.0	1.35	1.31	---
ORNL	96.9	10.66	6.0	0.09	0.18	---
ORNL	96.5	10.62	6.0	1.39	1.43	---
ORNL	97.3	10.70	6.0	0.32	0.25	---
ORNL	81.6	8.98	6.0	2.05	2.73	2.0364
ORNL	89.6	9.86	6.0	3.01	3.09	---
ORNL	91.2	9.81	6.0	1.57	1.52	2.0375
ORNL	84.9	9.34	6.0	10.25	8.33	2.2200
ORNL	96.0	10.56	6.0	7.63	7.26	---
ORNL	96.4	10.60	6.0	1.84	1.73	2.1700
ORNL	95.4	10.49	6.0	1.78	1.76	---
ORNL	91.1	10.02	6.0	0.68	1.62	2.0555
Davison (II)	93.2	10.25	4.0	---	26.1	---
Davison (II)	92.5	10.17	10.0	---	162.	---
NUMEC	95.7	10.53	14.0	---	14.6	---
NUMEC	94.8	10.43	14.0	---	13.3	---
NUMEC	94.2	10.36	14.0	---	10.5	---
United Nuclear	93.6	10.30	14.0	---	24.8	---
Atomics Int'l.	93.6	10.30	14.0	---	14.9	---

Table A-9. Dissolution Rates of PuO_2 Pellets in Nitric Acid, Hydrofluoric Acid, and Aluminum Nitrate

Pellet Density: 10.3 ± 0.1 g/cm^3

Concentration (M)			Instantaneous Dissolution Rate
HNO_3	HF	$Al(NO_3)_3$	(mg PuO_2 cm^{-2} min^{-1})
14.0	---	---	4.38×10^{-3}
10.0	---	---	1.03×10^{-3}
7.0	---	---	2.53×10^{-4}
7.0	0.005	---	1.72×10^{-3}
10.0	0.005	---	3.88×10^{-3}
14.0	0.005	---	2.88×10^{-2}
7.0	0.005	---	1.05×10^{-3}
14.0	0.005	---	2.68×10^{-2}
7.0	0.01	---	4.31×10^{-3}
10.0	0.01	---	1.13×10^{-2}
14.0	0.01	---	6.33×10^{-2}
7.0	0.01	---	2.84×10^{-3}
10.0	0.01	---	9.75×10^{-2}
14.0	0.01	---	6.07×10^{-2}
7.0	0.05	---	3.86×10^{-2}
10.0	0.05	---	1.14×10^{-1}
14.0	0.05	---	4.03×10^{-1}
7.0	0.05	---	3.71×10^{-2}
14.0	0.1	---	1.49
10.0	0.1	---	2.65×10^{-1}
7.0	0.1	---	9.16×10^{-2}
14.0	0.005	0.015	5.35×10^{-3}
10.0	0.005	0.015	1.40×10^{-3}
7.0	0.005	0.015	3.54×10^{-4}
14.0	0.01	0.03	9.82×10^{-3}
10.0	0.01	0.03	1.74×10^{-3}
7.0	0.01	0.03	4.42×10^{-4}
14.0	0.05	0.15	1.50×10^{-2}
10.0	0.05	0.15	2.74×10^{-3}
7.0	0.05	0.15	6.80×10^{-4}
14.0	0.1	0.3	1.67×10^{-2}
10.0	0.1	0.3	4.05×10^{-3}
7.0	0.1	0.3	9.09×10^{-4}
10.0	0.1	0.1	6.58×10^{-3}
10.0	0.1	0.2	4.67×10^{-3}

Table A-10. Dissolution Rates of PuO_2 Pellets in Nitric Acid Containing Ceric Ammonium Nitrate

Pellet Density: 10.3 ± 0.1 g/cm^3

HNO_3 Conc. (M)	Ce(IV) Conc. (M)	Instantaneous Dissolution Rate (mg PuO_2 cm^{-2} min^{-1})
2.0	0.5	3.72×10^{-2}
2.0	0.5	2.63×10^{-2}
2.0	0.1	1.55×10^{-2}
2.0	0.1	2.73×10^{-2}
2.0	0.01	9.89×10^{-3}
2.0	0.01	3.56×10^{-3}
7.0	0.1	9.09×10^{-3}
7.0	0.1	1.08×10^{-2}
7.0	0.1	7.78×10^{-3}
7.0	0.05	7.86×10^{-3}
7.0	0.05	4.42×10^{-3}
7.0	0.01	1.17×10^{-3}
7.0	0.01	6.16×10^{-4}
7.0	0.005	5.58×10^{-4}
7.0	0.005	5.62×10^{-4}
7.0	0.005	6.39×10^{-4}
7.0	0.001	8.15×10^{-4}
7.0	0.001	3.58×10^{-4}
7.0	0.001	3.51×10^{-4}
7.0	0.0005	3.67×10^{-4}
7.0	0.0005	6.07×10^{-4}
10.0	0.1	1.32×10^{-2}
10.0	0.1	4.96×10^{-3}
10.0	0.01	1.13×10^{-3}
10.0	0.01	1.26×10^{-3}
14.0	0.1	1.75×10^{-3}
14.0	0.1	4.48×10^{-3}
14.0	0.01	1.11×10^{-3}
14.0	0.01	1.29×10^{-3}
7.0	---	3.00×10^{-4}
10.0	---	9.24×10^{-4}
14.0	---	2.33×10^{-3}

Table A-11. Dissolution Rates of PuO_2 Pellets in Nitric Acid Containing Ozone

Pellet Density: 10.3 ± 0.1 g/cm^3

HNO_3 Conc. (N)	Addition of 6% O_3 Flow Rate (cfm)	Instantaneous Dissolution Rate (mg PuO_2 cm^{-2} min^{-1})
2.0	0.04	7.23×10^{-4}
2.0	0.04	8.36×10^{-4}
7.0	0.01	5.23×10^{-4}
7.0	0.01	1.51×10^{-4}
7.0	0.02	5.23×10^{-4}
7.0	0.02	1.64×10^{-4}
7.0	0.04	2.37×10^{-4}
7.0	0.04	2.12×10^{-4}
7.0	0.06	4.99×10^{-4}
7.0	0.06	1.82×10^{-4}
7.0	0.08	5.63×10^{-4}
7.0	0.08	4.67×10^{-4}
7.0	0.10	6.69×10^{-4}
7.0	0.14	2.89×10^{-4}
7.0	0.14	1.70×10^{-4}
10.0	0.04	1.37×10^{-3}
14.0	0.04	3.75×10^{-3}
14.0	0.04	4.96×10^{-3}

Table A-12. Dissolution Rates of PuO_2 Pellets in Nitric and Hydrochloric Acids

Pellet Density: 10.3 ± 0.1 g/cm^3

Concentration (M)		Instantaneous Dissolution Rate (mg PuO_2 cm^{-2} min^{-1})
HNO_3	HCl	
3	2	5.03×10^{-4}
5	5	4.67×10^{-4}
5	3	5.10×10^{-4}
5	2	8.36×10^{-4}
5	1	4.06×10^{-4}
5	0.5	3.24×10^{-4}
5	0.1	2.27×10^{-4}
6	2	1.15×10^{-3}
7	2	7.27×10^{-4}
10	2	4.57×10^{-4}

Table A-13. Effect of Density on the Rates of Dissolution of PuO_2 Pellets in 14 M HNO_3

Pellet Density (g/cm^3)	Pellet Density (% of Theo.)	Instantaneous Dissolution Rate ($mg\ PuO_2\ cm^{-2}\ min^{-1}$)
8.86	77.4	1.36×10^{-1}
8.97	78.4	1.43×10^{-1}
9.34	81.6	5.53×10^{-2}
9.56	83.6	1.24×10^{-1}
10.14	88.6	1.94×10^{-3}
10.22	89.3	5.71×10^{-3}
10.33	90.3	4.38×10^{-3}
10.33	90.3	4.76×10^{-3}
10.34	90.4	5.78×10^{-3}
10.34	90.4	5.70×10^{-3}
10.38	90.7	3.90×10^{-3}

Table A-14. Effect of Molar Excess of Nitric Acid on the Dissolution Time of UO_2 Pellets

Pellet Density: $10.3 \pm 0.1\ g/cm^3$

HNO_3 Conc. (M) Initial	HNO_3 Conc. (M) Final	Initial Ratio: M H^+ / M U	UO_2 Initial (g)	UO_2 Dissolved (g)	UO_2 Dissolved (%)	Acid Consumed (moles/mole UO_2 dissolved)		Diss. Time (min)
14.3	13.10	34	14.461	14.435	99	2.89		60
14.3	12.80	34	14.575	14.469	99	3.89		57
14.3	12.90	34	14.500	14.912	100	3.23		60
14.3	12.90	34	14.500	14.666	100	3.34	Ave. = 3.36	60
14.3	11.71	20	14.350	14.426	100	3.31		60
14.3	11.71	20	14.235	14.550	100	3.70		60
14.3	9.63	10	14.370	14.440	100	3.25		60
14.3	9.71	10	14.390	14.572	100	3.27		60
10.3	9.38	34	14.400	13.974	97	3.16		120
10.3	9.41	34	14.570	15.397	100	2.94		140
10.3	8.89	21	14.273	14.311	100	2.83	Ave. = 2.82	140
10.3	8.85	21	14.499	14.446	99	2.87		135
10.3	6.22	6.9	14.411	14.297	99	2.70		115
10.3	6.71	6.9	14.570	14.438	99	2.43		120
6.2	5.73	34	14.528	14.562	100	2.61		465
6.2	5.60	34	14.526	14.913	100	3.33		450
6.2	5.50	21	14.577	15.003	100	2.41		480
6.2	5.50	21	14.515	15.027	100	2.36	Ave. = 2.64	465
6.2	3.94	6.9	14.424	14.160	98	2.58		465
6.2	3.88	6.9	14.481	14.808	100	2.58		435
6.2	3.85	6.9	14.315	14.253	99	2.26		450
6.2	3.87	6.9	14.716	14.975	100	2.59		480

Table A-15. Variation in Effective Surface Area of a UO_2 Pellet Dissolving in 6 M HNO_3

Pellet Density: 10.3 ± 0.1 g/cm^3

Time (min)	UO_2 Dissolved (g)	UO_2 Dissolved (%)	Radius (cm)	Surface Area (cm^2)	Wt. Loss (g)	Weight Loss Rate (g/min)	Diss. Rate[a]	Roughening Factor, R_T/R_o	
Pellet initial weight, 14.538 grams									
3	0.175	1.20	0.530	7.05	0.175	0.058	0.0083	1.00	(0.463) Roughening Constant
5	0.293	2.03	0.527	7.03	0.118	0.059	0.0084	1.01	
10	0.652	4.52	0.525	7.0	0.359	0.072	0.0106	1.28	
15	1.087	7.53	0.520	6.8	0.435	0.087	0.0130	1.57	
20	1.641	11.36	0.514	6.7	0.554	0.111	0.0168	2.02	
25	2.192	15.18	0.505	6.6	0.551	0.110	0.0174	2.09	
30	2.861	19.81	0.497	6.3	0.669	0.134	0.0219	2.64	
40	4.146	28.71	0.490	6.1	1.281	0.128	0.0224	2.70	
50	5.234	36.25	0.467	5.7	1.088	0.109	0.0205	2.47	
60	6.829	47.30	0.448	5.3	1.595	0.160	0.0347	4.18	
75	8.558	59.27	0.422	4.6	1.731	0.115	0.0294	3.54	
90	10.103	69.97	0.378	3.9	1.545	0.103	0.0312	3.76	
120	11.909	82.48	0.334	3.3	1.806	0.060	0.0261	3.14	
165	13.118	90.85	0.267	2.3	1.209	0.027	0.0169	2.03	
275	13.810	95.64	0.203	1.6	0.692	0.006	0.0060		
360	14.274	98.86	0.151	1.0	0.464	0.005	0.0008		
405	14.603	99.4	0.072	0.6	0.339	0.008			
Pellet initial weight, 14.485 grams									
3	0.175	1.21	0.530	7.0	0.175	0.058	0.0083	1.00	(0.475) Roughening Constant
5	0.387	2.67	0.527	6.9	0.212	0.106	0.0154	1.86	
10	0.768	5.30	0.524	6.8	0.381	0.076	0.0112	1.35	
15	1.129	7.79	0.518	6.6	0.361	0.072	0.0109	1.31	
20	1.548	10.69	0.513	6.5	0.419	0.084	0.0129	1.55	
25	1.845	12.74	0.507	6.4	0.297	0.059	0.0092	1.11	
30	2.265	15.64	0.502	6.3	0.420	0.084	0.0133	1.60	
40	3.001	20.72	0.497	6.0	0.736	0.074	0.0123	1.48	
50	3.914	27.02	0.485	5.7	0.913	0.091	0.0160	1.93	
60	5.100	35.21	0.470	5.3	1.186	0.119	0.0225	2.71	
75	7.125	49.19	0.450	4.5	2.025	0.135	0.0300	3.61	
90	8.887	61.35	0.413	3.8	1.762	0.117	0.0308	3.71	
120	11.370	78.49	0.371	2.6	2.483	0.083	0.0319	3.84	
165	13.020	89.88	0.290	1.6	1.650	0.037	0.0231	2.78	
225	14.130	97.55	0.210	0.68	1.110	0.019	0.0279	3.36	
300	14.355	99.10	0.115	0.38	0.225	0.003	0.0079		
390	14.450	99.6	0.065		0.095	0.001			

[a]Surface calculated from percentage of pellet dissolved. Rate expressed as g cm^{-2} min^{-1}.

Table A-16. Variation in Effective Surface Area of a UO_2 Pellet Dissolving in 10 M HNO_3

Pellet Density: 10.3 ± 0.1 g/cm^3

Time (min)	UO_2 Dissolved (g)	UO_2 Dissolved (%)	Radius (cm)	Surface Area (cm^2)	Weight Loss (g)	Weight Loss Rate (g/min)	Diss. Rate[a]	Roughening Factor R_t/R_i	
Pellet initial weight, 14.589 grams									
1	0.165	1.13	0.530	7.05	0.165	0.165	0.0234	1.00	(0.389) Roughening Constant
2	0.518	3.6	0.527	6.9	0.353	0.353	0.0512	2.19	
4	1.314	9.0	0.522	6.65	0.796	0.398	0.0598	2.56	
7	2.521	17.3	0.511	6.22	1.207	0.402	0.0646	2.76	
10	3.626	24.9	0.494	5.82	1.105	0.368	0.0632	2.70	
15	5.257	36.0	0.476	5.23	1.629	0.326	0.0623	2.66	
20	7.009	48.0	0.449	4.55	1.752	0.350	0.0769	3.29	
25	8.676	59.5	0.415	3.87	1.667	0.333	0.0860	3.68	
30	10.260	70.3	0.377	3.20	1.584	0.317	0.0991	4.24	
40	12.496	85.7	0.332	2.00	2.236	0.224	0.112	4.78	
50	13.582	93.1	0.242	1.30	1.086	0.109	0.0838	3.58	
60	13.947	95.6	0.185	1.00	0.365	0.037	0.0372	1.59	
75	14.315	98.1	0.150	0.55	0.368	0.025	0.0455	1.94	
90	14.401	98.7	0.100	0.42	0.086	0.006	0.0143	0.61	
105	14.484	99.3	0.082	0.25	0.083	0.005	0.0200	0.85	
120	14.590	99.5	0.060	--	0.106	0.007	--	--	
Pellet initial weight, 14.539 grams									
1	0.165	1.13	0.530	7.02	0.165	0.165	0.0235	1.00	(0.384) Roughening Constant
2	0.630	4.3	0.528	6.88	0.465	0.465	0.0676	2.88	
4	1.392	9.6	0.525	6.60	0.762	0.381	0.0577	2.46	
7	2.469	17.0	0.510	6.22	1.077	0.359	0.0577	2.46	
10	3.249	22.3	0.495	5.95	0.780	0.260	0.0437	1.86	
15	4.691	32.3	0.482	5.43	1.442	0.288	0.0530	2.26	
20	6.313	43.4	0.457	4.82	1.622	0.324	0.0672	2.86	
30	9.498	65.3	0.426	3.52	3.185	0.319	0.0906	3.86	
40	11.893	81.8	0.355	2.33	2.395	0.240	0.103	4.38	
60	13.913	95.7	0.270	0.903	2.020	0.101	0.112	4.77	
75	14.274	98.2	0.148	0.500	0.361	0.024	0.0480	2.04	
105	14.391	99.0	0.095	0.35	0.117	0.004	0.0114	0.49	
140	14.548	99.4	0.080	--	0.157	0.004	--	--	

[a]Surface calculated from percentage of pellet dissolved. Rate expressed as g cm^{-2} min^{-1}.

Table A-17. Variation in Effective Surface Area of a UO_2 Pellet Dissolving in 14 M HNO_3

Pellet Density: 10.3 ± 0.1 g/cm^3

Time (min)	UO_2 Dissolved (g)	UO_2 Dissolved (%)	Radius (cm)	Surface Area (cm^2)	Weight Loss (g)	Weight Loss Rate (g/min)	Diss. Rate[a]	Roughening Factor R_t/R_i	
Pellet initial weight, 14.332 grams									
0.5	0.163	1.14	0.530	7.05	0.163	0.326	0.0462	1.00	(0.379) Roughening Constant
1	0.456	3.2	0.527	6.92	0.293	0.586	0.0847	1.83	
3	1.573	11.0	0.522	6.55	1.117	0.558	0.0852	1.84	
5	2.786	19.4	0.506	6.10	1.213	0.606	0.0993	2.15	
7	4.456	31.1	0.490	5.49	1.670	0.823	0.150	3.27	
10	6.660	46.5	0.461	4.65	2.204	0.735	0.158	3.42	
15	10.460	73.0	0.420	3.00	3.800	0.760	0.253	5.48	
20	12.451	86.9	0.320	1.95	1.991	0.398	0.204	4.42	
25	13.402	93.5	0.235	1.25	0.951	0.190	0.152	3.29	
35	13.775	96.1	0.178	0.80	0.373	0.037	0.0463	1.00	
55	14.302	99.9	0.142	--	0.527	0.026	--	--	
Pellet initial weight, 14.615 grams									
0.5	0.165	1.1	0.530	7.05	0.165	0.328	0.0465	1.00	(0.499) Roughening Constant
1	0.335	2.3	0.527	6.98	0.171	0.342	0.0490	1.05	
3	1.476	10.1	0.525	6.60	1.141	0.571	0.0865	1.86	
5	2.498	17.1	0.508	6.22	1.022	0.511	0.0822	1.77	
7	3.580	24.5	0.495	5.83	1.082	0.541	0.0928	2.00	
10	5.464	37.4	0.477	5.14	1.884	0.628	0.122	2.62	
15	8.772	60.0	0.445	3.86	3.308	0.661	0.171	3.68	
20	11.269	77.1	0.372	2.71	2.496	0.499	0.184	3.96	
25	12.848	87.9	0.300	1.82	1.579	0.316	0.174	3.74	
30	13.775	94.3	0.225	1.13	0.927	0.185	0.164	3.53	
35	14.034	96.0	0.170	0.90	0.259	0.052	0.0578	1.24	
45	14.214	97.3	0.144	0.67	0.180	0.018	0.0269	0.578	
55	14.434	98.8	0.123	0.37	0.220	0.022	0.0594	1.28	
65	14.528	99.4	0.075	0.25	0.094	0.009	0.0360	0.774	
75	14.653	99.9	0.052	--	0.125	0.013	--	--	

[a]Surface calculated from percentage of pellet dissolved. Rate expressed as g cm^{-2} min^{-1}.

Table A-18. Variation in Apparent Dissolution Rate of a Davison II Pellet Dissolving in 4 M HNO_3

Pellet Density: 10.3 g/cm^3
Pellet initial weight, 15.885 grams

Time (min)	UO_2 Dissolved (g)	UO_2 Dissolved (%)	Surface Area[a] (cm^2)	Weight Loss (g)	Dissolution Rate, by Weight Loss (g/min)	Dissolution Rate, by Weight Loss (g cm^{-2} min^{-1})
0.5	0.098	0.62	7.00	0.098	0.196	0.0280
4	0.311	1.96	6.94	0.213	0.061	0.0088
8	0.466	2.93	6.72	0.155	0.039	0.0056
13	0.653	3.92	6.88	0.187	0.037	0.0054
18	0.850	5.35	6.80	0.197	0.039	0.0057
23	1.057	6.65	6.74	0.207	0.041	0.0061
30	1.338	8.42	6.68	0.281	0.040	0.0060
40	1.733	10.91	6.60	0.395	0.040	0.0061
50	2.225	14.01	6.45	0.492	0.049	0.0076
60	2.584	16.27	6.25	0.349	0.036	0.0058
71	3.194	20.11	6.10	0.610	0.055	0.0090
80	3.652	22.99	5.90	0.458	0.051	0.0096
100	4.332	27.27	5.75	0.680	0.034	0.0059
130	6.541	41.18	4.95	2.209	0.073	0.0147
162	8.141	51.25	4.40	1.600	0.050	0.0114
181	9.197	57.90	4.00	1.058	0.057	0.0143
195	9.817	61.80	3.75	0.620	0.046	0.0123
225	11.122	70.02	3.20	1.305	0.044	0.0138
240	11.600	73.02	3.00	0.478	0.032	0.0107
255	12.140	76.42	2.80	0.540	0.036	0.0129
270	12.346	77.72	2.60	0.206	0.014	0.0054
285	12.552	79.02	2.55	0.206	0.014	0.0053
325	13.258	83.46	2.20	0.706	0.018	0.0082

[a]Surface area calculated from percentage of pellet dissolved.

Table A-19. Variation in Apparent Dissolution Rate of a Davison II Pellet Dissolving in 10 M HNO_3

Pellet Density: 10.3 g/cm^3
Pellet initial weight, 14.029 grams

Time (min)	UO_2 Dissolved (g)	UO_2 Dissolved (%)	Surface Area[a] (cm^2)	Weight Loss (g)	Dissolution Rate, by Weight Loss (g/min)	Dissolution Rate, by Weight Loss (g cm^{-2} min^{-1})
0.25	0.282	2.01	7.00	0.282	1.128	0.161
1.50	0.630	4.49	6.86	0.348	0.278	0.0405
2.75	1.005	7.16	6.72	0.375	0.300	0.0446
4	1.332	9.49	6.61	0.327	0.262	0.0394
6	1.851	13.19	6.43	0.519	0.259	0.0403
8	2.420	17.25	6.20	0.569	0.284	0.0458
10.5	3.158	22.51	5.95	0.738	0.295	0.0496
12.5	3.859	27.51	5.67	0.701	0.350	0.0617
15	4.749	33.85	5.35	0.890	0.356	0.0665
17.5	5.626	40.10	5.00	0.877	0.351	0.0702
20	6.486	46.23	4.62	0.860	0.344	0.0745
23	7.741	55.18	4.13	1.255	0.418	0.101
26	8.678	61.86	3.74	0.937	0.312	0.0834
30	9.971	71.07	3.14	1.293	0.323	0.103
35	11.515	82.08	2.31	1.644	0.329	0.142
40	12.687	90.43	1.57	1.172	0.234	0.149
45	13.256	94.49	1.10	0.569	0.114	0.104
50	13.718	97.78	0.60	0.462	0.092	0.153
60	13.855	98.76	0.40	0.137	0.014	0.0350
80	13.920	99.22	0.30	0.065	0.003	0.0300
90	13.974	99.61	0.17	0.054	0.005	0.0294

[a]Surface area calculated from percentage of pellet dissolved.

Table A-20. Variation in the Apparent Dissolution Rate of an Atomics International UO_2 Pellet Dissolving in 4 M HNO_3

Pellet Density: 10.3 g/cm^3
Pellet initial weight, 6.2 grams

Time (min)	UO_2 Dissolved (g)	UO_2 Dissolved (%)	Surface Area[a] (cm^2)	Weight Loss (g)	Dissolution Rate, by Weight Loss (g/min)	Dissolution Rate, by Weight Loss (g cm^{-2} min^{-1})
0.75	0.044	0.71	3.95	0.044	0.059	0.015
2.0	0.239	3.85	3.80	0.195	0.156	0.041
3.5	0.658	10.60	3.70	0.419	0.279	0.075
5.0	1.233	19.86	3.40	0.575	0.383	0.113
7.0	2.029	32.67	3.05	0.796	0.398	0.131
9	2.829	45.56	2.63	0.800	0.400	0.153
12	3.808	61.32	2.10	0.979	0.326	0.155
15	4.562	73.46	1.62	0.754	0.251	0.155
18	5.188	83.54	1.18	0.626	0.209	0.177
21	5.597	90.13	0.85	0.409	0.136	0.160
24	5.805	93.48	0.64	0.208	0.069	0.108
27	5.986	96.39	0.43	0.181	0.060	0.140
45	6.157	99.14	0.18	0.171	0.010	0.056
60	6.177	99.47	0.12	0.020	0.002	0.017

[a]Surface area calculated from percentage of pellet dissolved.

Table A-21. Variation in the Apparent Dissolution Rate of an United Nuclear UO_2 Pellet Dissolving in 14 M HNO_3

Pellet Density: 10.30 g/cm^3
Pellet initial weight, 8.549 grams

Time (min)	UO_2 Dissolved (g)	UO_2 Dissolved (%)	Surface Area[a] (cm^2)	Weight Loss (g)	Dissolution Rate, by Weight Loss (g/min)	Dissolution Rate, by Weight Loss (g cm^{-2} min^{-1})
0.5	0.062	0.73	3.30	0.062	0.124	0.038
2.0	0.192	2.25	3.20	0.130	0.087	0.027
3.75	0.382	4.47	3.15	0.190	0.109	0.035
5.50	0.689	8.06	3.05	0.307	0.214	0.070
7.50	1.139	13.32	2.95	0.450	0.225	0.076
10.0	1.944	22.74	2.75	0.805	0.322	0.117
13.0	3.099	36.25	2.45	1.155	0.385	0.157
15.0	3.834	44.85	2.25	0.735	0.368	0.164
17.5	4.832	56.52	1.95	0.998	0.399	0.205
20	5.850	68.34	1.60	1.022	0.409	0.256
23	6.721	78.62	1.28	0.871	0.290	0.227
26	7.357	86.06	0.97	0.636	0.212	0.219
30	7.890	92.29	0.67	0.533	0.133	0.199
50	8.312	97.23	0.36	0.422	0.021	0.058
70	8.329	97.43	0.34	0.017	0.001	0.003

[a]Surface area calculated from percentage of pellet dissolved.

Table A-22. Variation in the Effective Surface Area of a PuO_2 Pellet Dissolving in 14 M HNO_3--0.05 M HF

Pellet Density: 10.3 g/cm^3
Pellet initial weight, 2.060 grams

Time (hr)	PuO_2 Dissolved (mg)	PuO_2 Dissolved (%)	Surface Area[a] (cm^2)	Weight Loss (mg)	Dissolution Rate, by Weight Loss (g/min)	Dissolution Rate, by Weight Loss (g cm^{-2} min^{-1})
1	34	1.67	1.85	34	0.57	0.31
2	75	3.64	1.83	41	0.68	0.37
5	145	7.02	1.80	70	0.38	0.21
10	287	13.93	1.70	142	0.47	0.28
15	412	19.99	1.60	125	0.42	0.26
20	533	25.88	1.52	121	0.40	0.26
25	647	31.43	1.45	114	0.38	0.26
30	729	35.39	1.40	82	0.27	0.19
35	854	41.45	1.31	125	0.42	0.32
40	938	45.53	1.26	84	0.28	0.22
45	1045	50.74	1.16	107	0.35	0.30
50	1137	55.21	1.10	92	0.30	0.27
55	1218	59.12	1.02	81	0.27	0.26
60	1273	61.78	0.98	65	0.22	0.22
65	1451	70.44	0.84	178	0.63	0.75
70	1512	73.39	0.78	61	0.20	0.26
75	1582	76.78	0.71	70	0.23	0.32
78	1616	78.43	0.68	34	0.18	0.26
82	1678	81.48	0.62	62	0.25	0.40
86	1744	84.65	0.56	66	0.27	0.48

[a]Rate based on surface calculated from Fig. 25.

6.2 FORTRAN Codes for Calculating Pellet Dimensions During Dissolution

1) FØRTRAN Code for calculating the radius and surface area of uniformly dissolving right cylinders when the height of the original cylinder is equal to or less than twice the radius.

```
        PROGRAM DISSØLVE
        DIMENSION CØ(4), HEIGHT (3)
  5     READ (50,6) RATIØ, HGTZERØ, PERCENT
  6     FORMAT (3 E12.7)
        CØ(1) = 1./ (HGTZERØ*HGTZERØ*HGTZERØ)
        CØ(2) = (4.*RATIØ-2.)/(HGTZERØ*HGTZERØ)
        CØ(3) = (4.*RATIØ*RATIØ-4.*RATIØ+1.)/HGTZERØ
        CØ(4) = -4.*RATIØ*RATIØ*PERCENT
        CALL VIETA (CØ, HEIGHT, MRQ1)
134     SURFACE = 1.57079632*(3.*HEIGHT*HEIGHT+4.*(2.*RATIØ-1.)
                  *HGTZERØ*HEIGHT+(2.*RATIØ-1.)*(2.*RATIØ-1.)*HGTZERØ*HGTZERØ)
 60     WRITE (50.7) RATIØ, HGTZERO, PERCENT, HEIGHT (1), SURFACE, MRQ1
  7     FORMAT (7HORATØ F6.3, 2x8 HHGTZERØ F7.4, 2x8 HPERCENT F7.4, 2x10
              HHEIGHT(T) F7.4, 2x8 HSURFACE F8.4, 2x5 HMRQ1 13/)
        GØ TO 5
        END DISSOLVE
```

2) FØRTRAN Code for calculating the height and surface area of a uniformly dissolving right cylinder when the height is greater than twice the radius.

```
        PRØGRAM DISSØLVE
        DIMENSIØN (CØ(4), RADI(3)
  5     READ (50.6) RATIØ, RADZERØ, PERCENT
  6     FØRMAT (3E12.7)
        CØ(1) = 2./(RATIØ*RADZERØ*RADZERØ*RADZERØ)
        CØ(2) = (RATIØ-2.)/(RATIØ*RADZERØ*RADZERØ)
        CØ(3) = 0.
        CØ(4) = -PERCENT
        CALL VIETA (CØ, RADI, MRØ1)
```

```
134     SURFACE = 6.2831853*RADT (1)*(3.*RADT(1)+RADZERØ*(RATIØ-2.))
 60     WRITE (51,7)RATIØ, RADZERØ, PERCENT, RADT (1), SURFACE= MRØI
  7     FORMAT (7HORATIØ F6.3, 2x8 HRADZERØ F7.4, 2x8 HPERCENT F7.4, 2x10
              HRADIUS 1(T) F7.4, 2x8 HSURFACE F8.4, 2x5 HMRØ I 13/)
        GØ TØ 5
        END DISSOLVE
```

The subroutine for the general solution of the cubic equations encountered in these programs is given below.

```
C2 UCSD VIETA    EXPLICIT SOLUTION OF THE GENERAL CUBIC
      SUBROUTINE VIETA(A,Y,MTYPE)
C     C2 UCSD VIETA
C     EXPLICIT SOLUTION OF THE GENERAL CUBIC EQUATION
      DIMENSION A(4), B(3), Y(3)
      B(1)=A(2)/A(1)
      B1OV3=B(1)/3.0
      B(2)=A(3)/A(1)
      B(3)=A(4)/A(1)
      ALF=B(2)-B(1)*B1OV3
      BET=2.0*B1OV3**3-B(2)*B1OV3+B(3)
      BETOV2=BET/2.0
      ALFOV3=ALF/3.0
      CUAOV3=ALFOV3**3
      SQBOV2=BETOV2**2
      DEL=SQBOV2+CUAOV3
      IF(DEL)40,20,30
20    MTYPE=0
      GAM=SQRTF(-ALFOV3)
      IF(BET)22,22,21
21    Y(1)=-2.0*GAM-B1OV3
      Y(2)=GAM-B1OV3
      Y(3)=Y(2)
      GO TO 50
```

```
      Y(1)=2.0*GAM-B1OV3
      Y(2)=-GAM-B1OV3
      Y(3)=Y(2)
      GO TO 50
30    MTYPE=1
      EPS=SQRTF(DEL)
      TAU=-BETOV2
      R=CUBERTF(TAU+EPS)
      S=CUBERTF(TAU-EPS)
      Y(1)=R+S-B1OV3
      Y(2)=-(R+S)/2.0-B1OV3
      Y(3)=0.86602540*(R-S)
      GO TO 50
40    MTYPE=-1
      QUOT=SQBOV2/CUAOV3
      ROOT=SQRTF(-QUOT)
      IF(BET)42,41,41
41    PHI=(1.5707963+ASINF(ROOT))/3.0
      GO TO 43
42    PHI=ACOSF(ROOT)/3.0
43    FACT=2.0*SQRTF(-ALFOV3)
      Y(1)=FACT*COSF(PHI)-B1OV3
      Y(2)=FACT*COSF(PHI+2.0943951)-B1OV3
      Y(3)=FACT*COSF(PHI+4.1887902)-B1OV3
50    RETURN
C     THIS IS THE LAST CARD OF VIETA SUBROUTINE
      END
      FUNCTION CUBERTF(X)
      IF(X)2,3,4
2     X=-X
      CUBERTF=-X**.333333333333
      RETURN
```

```
3     CUBERTF=0.
      RETURN
4     CUBERTF=X**.333333333333
      RETURN
      END
```

ORNL-3695
UC-4 – Chemistry
TID-4500 (37th ed.)

INTERNAL DISTRIBUTION

1. Biology Library
2-4. Central Research Library
5. Reactor Division Library
6-7. ORNL – Y-12 Technical Library
Document Reference Section
8-42. Laboratory Records Department
43. Laboratory Records, ORNL R.C.
44. R. E. Blanco
45. E. S. Bomar
46. F. L. Culler
47. D. E. Ferguson
48. L. M. Ferris
49. H. E. Goeller
50. C. E. Lamb
51. C. E. Larson
52. R. E. Leuze
53. H. G. MacPherson
54-63. R. H. Rainey
64. M. J. Skinner
65-102. D. B. Trauger
103-112. A. Uriarte
113. K. S. Warren
114. A. M. Weinberg
115-134. G. D. Whitman
135. P. H. Emmett (consultant)
136. J. J. Katz (consultant)
137. C. W. J. Wende (consultant)
138. C. E. Winters (consultant)

EXTERNAL DISTRIBUTION

139. H. Schneider, U.S. Atomic Energy Commission, Washington
140. E. L. Anderson, U.S. Atomic Energy Commission, Washington
141. O. T. Roth, U.S. Atomic Energy Commission, Washington
142. J. A. Buckham, Phillips Petroleum Company
143. L. P. Hatch, Brookhaven National Laboratory
144. A. M. Platt, Hanford Atomic Products Operation
145. R. E. Tomlinson, Hanford Atomic Products Operation
146. M. T. Walling, Hanford Atomic Products Operation
147. O. F. Hill, Hanford Atomic Products Operation
148. C. H. Ice, Du Pont Company, Aiken
149. L. H. Meyer, Du Pont Company, Aiken
150. D. S. Webster, Du Pont Company, Aiken
151. S. Lawroski, Argonne National Laboratory
152. W. H. Swift, Hanford Atomic Products Operation
153. J. M. Cleveland, Dow Chemical Company, Rocky Flats
154. H. W. Alter, Vallecitos Atomic Laboratory
155. K. H. Puechl, Nuclear Materials and Equipment Company, Leechburg, Pennsylvania
156. W. H. Lewis, Davison Chemical Company, Erwin, Tennessee
157. S. L. Reese, Nuclear Fuel Services, Springville, New York
158. Research and Development Division, AEC, ORO
159-756. Given distribution as shown in TID-4500 (37th ed.) under Chemistry category (75 copies – CFSTI)