MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0361487 2

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

4

ORNL-2934
UC-80 - Reactors-General

SULFEX-THOREX AND DAREX-THOREX PROCESSES FOR THE DISSOLUTION OF CONSOLIDATED EDISON POWER REACTOR FUEL: LABORATORY DEVELOPMENT

L. M. Ferris
A. H. Kibbey

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

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

Printed in USA. Price $0.75. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D.C.

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-2934

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

CHEMICAL DEVELOPMENT SECTION B

SULFEX-THOREX AND DAREX-THOREX PROCESSES FOR THE DISSOLUTION OF CONSOLIDATED EDISON POWER REACTOR FUEL: LABORATORY DEVELOPMENT

L. M. Ferris

A. H. Kibbey

Technician

J. F. Land

DATE ISSUED

OCT 26 1960

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
for the
U. S. ATOMIC ENERGY COMMISSION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0361487 2

ABSTRACT

Modified flowsheets, based on laboratory-scale studies, are presented for batch dissolution of Consolidated Edison power reactor fuel. The stainless steel jacket may be dissolved in either boiling 5 M HNO_3—2 M HCl (Darex process) or boiling 6 M H_2SO_4 (Sulfex process). In each case a waste solution containing about 50 g of stainless steel per liter is formed. With ThO_2-UO_2 core pellets, whose density is about 90% of theoretical, the uranium lost during decladding is expected to be less than 0.1% with either method. The high-density fuel pellets will be dissolved in 200% excess of boiling 13 M HNO_3—0.04 M NaF containing 0.04 or 0.1 M $Al(NO_3)_3$ after decladding by the Darex or Sulfex processes, respectively. Core dissolution will require at least 25 hr and will yield a solution containing about 1 M thorium and about 9 M HNO_3. The dissolution time could be shortened slightly by decreasing the aluminum concentration in the dissolvent or by adding about 0.5 M $Fe(NO_3)_3$. Sulfate ion, which might be present after Sulfex decladding, decreased the core dissolution rate. The rate of dissolution of the fuel pellets was inversely proportional to the density of the pellets; the initial 10-min rate of dissolution in boiling 13 M HNO_3-0.04 M NaF-0.1 M $Al(NO_3)_3$ of 95% ThO_2-5% UO_2 pellets decreased from about 16 to 2 mg $min^{-1}cm^{-2}$ as the pellet density increased from 60 to 94% of theoretical.

The solubility of stainless steel in sulfuric acid at 25°C decreased from 80 to 40 g/liter as the acidity increased from 4 to 10 N.

CONTENTS

		Page
1.0	Introduction	4
2.0	Flowsheets	4
	2.1 Darex-Thorex Process	4
	2.2 Sulfex-Thorex Process	6
3.0	Experimental Work	8
	3.1 Solubility of Stainless Steel in Sulfuric Acid	8
	3.2 Variables Affecting Uranium Losses During Sulfex Decladding	10
	3.3 Variables Affecting Rate of Core Dissolution	13
	3.4 Flowsheet Demonstration Experiments	21
	3.5 Passivation Studies	24
	3.6 Off-Gases	25
4.0	References	26

1.0 INTRODUCTION

This report summarizes laboratory data obtained at ORNL between June 1959 and Jan. 1, 1960 in the development of batch processes for the dissolution of Consolidated Edison power reactor fuel. This fuel will be sintered ThO_2-UO_2 pellets, nominally 93% of theoretical density, with the UO_2 content ranging from 2 to 8 wt %.[1] The pellets will be about 2.1 cm long with a diameter of about 0.66 cm. The cladding will be 304 stainless steel (20 mils thick). The investigations were on decladding by the Darex[2] (dilute aqua regia) and Sulfex[3] (4-6 M H_2SO_4) processes and dissolution of the core in boiling 13 M HNO_3—0.04 M NaF (the Thorex reagent) containing 0.04 or 0.1 M $Al(NO_3)_3$, depending on the decladding procedure. The higher aluminum concentration is required to suppress corrosion of the Sulfex Ni-o-nel dissolver, while only 0.04 M $Al(NO_3)_3$ affords adequate protection of the Darex titanium dissolver.[4] Both processes will probably be tested on the pilot plant scale. The Darex process seems superior from most viewpoints, but enough uncertainty exists to warrant parallel development of the Sulfex process.

Advantages of the Sulfex process are that Ni-o-nel is less expensive than titanium and that no further treatment of the decladding waste solution other than neutralization is required. However, the decladding waste volumes are very large and the presence of sulfate complicates waste treatment methods. On the other hand, use of the Darex process avoids the handling of large quantities of hydrogen and the problems that can be created by cross-contamination of solutions in the Sulfex-Thorex process, and decreases the probability of passivation in the decladding step. A disadvantage is the necessity of handling large amounts of chloride in the head-end system. Uranium losses and the volumes of decladding waste solution generated are about the same for each process. However, chloride must be removed before the Darex clad solution is flushed to the waste system. In the event of high uranium losses during decladding, which might be the case if the fuel pellets shatter severely during irradiation, the uranium is readily recovered from the chloride-free Darex waste by a single contact with 30% TBP in Amsco.[5] The use of 0.1 M $Al(NO_3)_3$ in the core dissolvent after Sulfex decladding leads to a lower rate of core dissolution than can be obtained with the 0.04 M aluminum after Darex decladding.

The authors wish to thank K. S. Warren of the ORNL Chemical Technology Division for his study of the solubility of stainless steel in sulfuric acid. Chemical and x-ray analyses were made by the groups of G. R. Wilson, W. R. Laing, and R. L. Sherman of the ORNL Analytical Chemistry Division.

2.0 FLOWSHEETS

2.1 Darex-Thorex Process

The 20-mil stainless steel cladding[1] is dissolved in about 3 hr in sufficient boiling dilute aqua regia, 5 M HNO_3—2 M HCl, to yield a solution containing about 50 g of stainless steel per liter (Fig. 1). Water used to

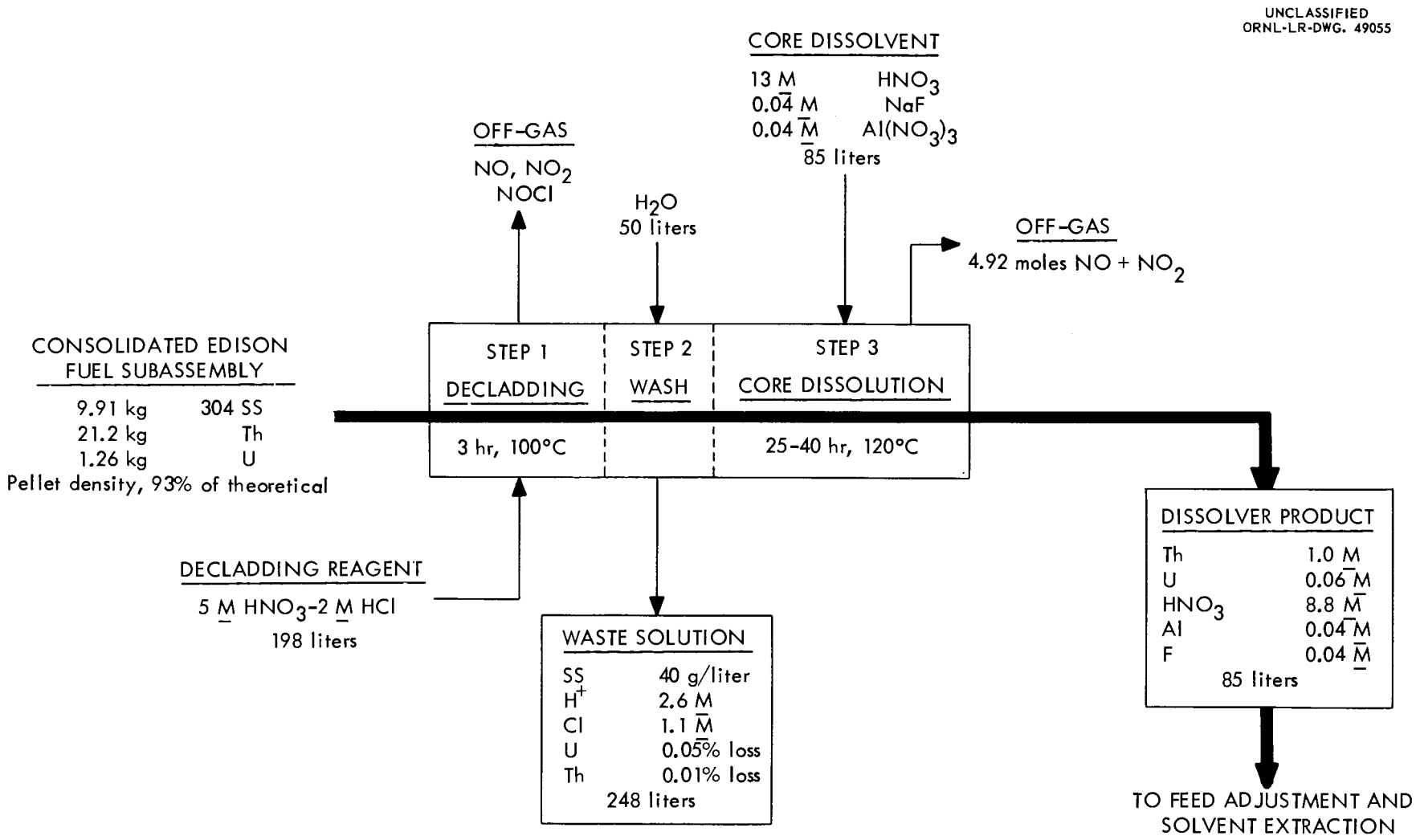

Fig. 1. Decladding and dissolution of Consolidated Edison reactor fuel by the Darex-Thorex process.

rinse out the vessel after decladding is combined with the clad solution to produce a waste solution containing about 40 g of stainless steel per liter. Soluble uranium losses from fuel pellets of greater than 90% of theoretical density are expected to be less than 0.1%; however, if losses are higher, virtually all the uranium can be recovered by contacting the clad solution, once it is freed of chloride, with 30% TBP in Amsco.[5] In any event, the chloride must be removed before the waste solution is neutralized and jetted to stainless steel storage tanks. Nitric and hydrochloric acids can be recovered by condensing the gases evolved during decladding and chloride removal.

Complete batch dissolution of the core in boiling 13 M HNO_3--0.04 M NaF--0.04 M $Al(NO_3)_3$ will probably require a minimum of 25 hr if the density of the pellets is greater than 90% of theoretical. A minimum of 200% stoichiometric excess* of acid will be required. Repeated digestions with fresh dissolvent may decrease the time required for complete dissolution but will give a more dilute product. Under the conditions shown in the flowsheet, the product contains 1 M thorium and about 9 M HNO_3. Thorium and uranium may be separated and decontaminated from fission products by any of several solvent extraction processes.[6]

2.2 Sulfex-Thorex Process

The 20-mil stainless steel cladding is dissolved in about 6 hr in a minimum of 200% excess of boiling 6 M H_2SO_4 (Fig. 2). Ideally, the reaction would be initiated with boiling 6 M H_2SO_4 and the solution diluted to 4 M sulfate shortly thereafter. This technique results in less corrosion of the dissolver and minimizes the possibility of precipitation of stainless steel sulfates during decladding. However, in cases where stainless steel is passive even to boiling 6 M H_2SO_4, it may be necessary to initiate the reaction with 12 M H_2SO_4,[7] a technique which results in severe corrosion of Ni-o-nel.[8] Ultimately, a waste solution containing about 55 g of stainless steel per liter will be produced. The uranium loss to the decladding solution should be less than 0.1% if the density of the core pellets is greater than 90% of theoretical.

After the decladding step the dissolver must be washed clean of sulfate to avoid complications during core dissolution (Sect. 3.3.6). The method of core dissolution is identical with that used after Darex decladding except that the aluminum concentration in the dissolvent must be about 0.1 M to prevent excessive corrosion of the Ni-o-nel dissolver. The dissolver must be washed thoroughly after core dissolution to prevent contamination of the next decladding solution with nitrate. As little as 0.01 M nitrate in 6 M H_2SO_4 can cause passivation of 304 stainless steel.[3,7,9] Probably, the sulfuric acid will be made 0.1 M in formic acid to ensure destruction of the last traces of nitrate.[7]

---

*Acid excesses are computed from the reactions

$$ThO_2 + 4\ HNO_3 \longrightarrow Th(NO_3)_4 + 2\ H_2O$$

$$2\ UO_2 + 6\ HNO_3 \longrightarrow 2\ UO_2(NO_3)_2 + NO + NO_2 + 3\ H_2O$$

assuming the pellets to be 95% ThO_2.

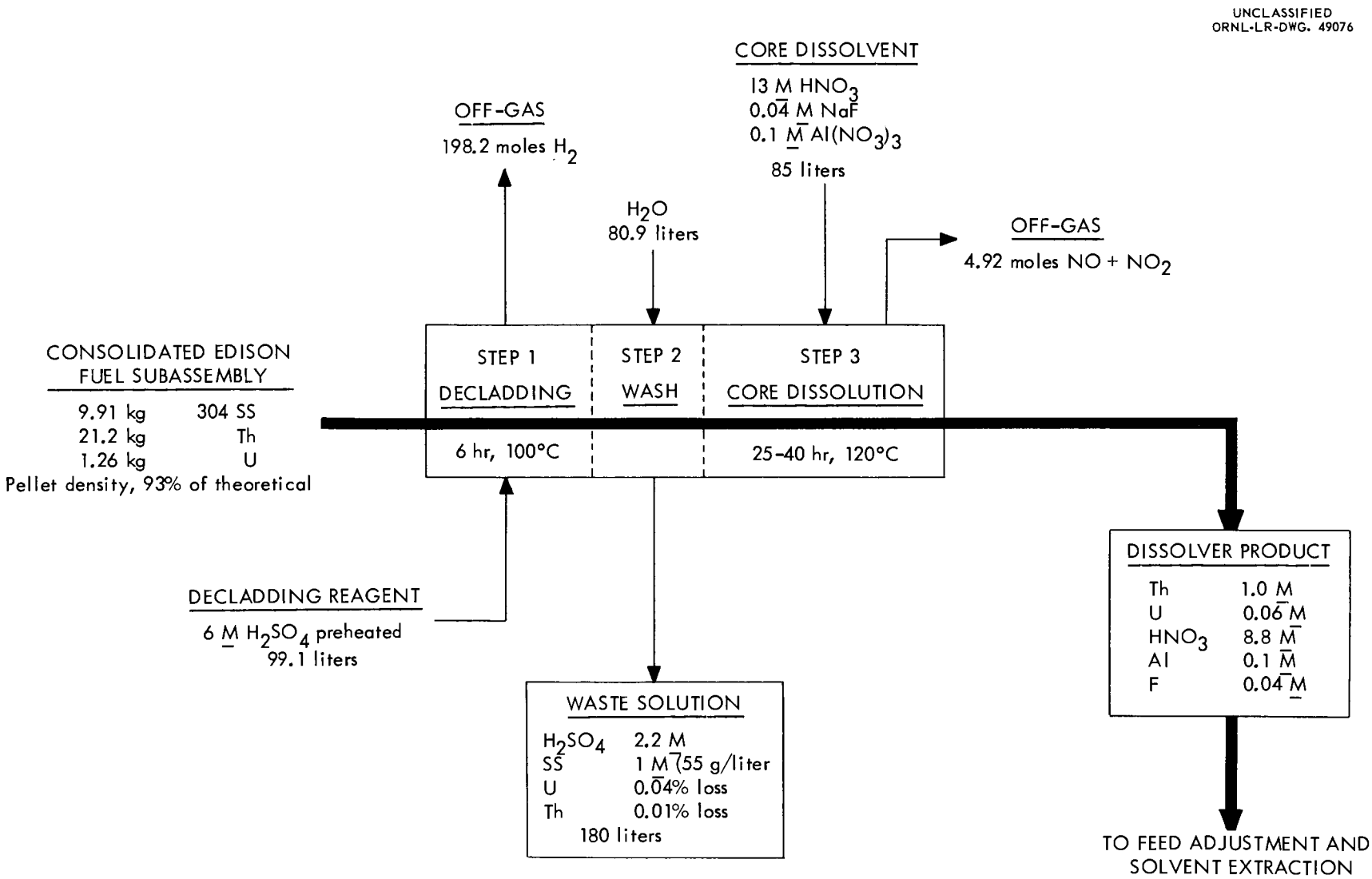

Fig. 2. Decladding and dissolution of Consolidated Edison reactor fuel by the Sulfex-Thorex process.

3.0 EXPERIMENTAL WORK

3.1 Solubility of Stainless Steel in Sulfuric Acid

At 25°C the solubility of stainless steel in sulfuric acid decreased from 80 to 10 g/liter as the acidity was increased from 4 to 15 N (Table 1, Fig. 3). The minimum waste volume is determined by the solubility regardless of whether the dissolution is carried out batchwise or continuously. Six molar acid was selected as the dissolvent in the process to produce higher dissolution rates and minimize passivation.

Table 1. Solubility of Stainless Steel in Sulfuric Acid at 25°C

Stainless steel dissolved in boiling 6-16 N H_2SO_4 and solutions cooled to room temperature; analyses made only of solutions in which no precipitation occurred

H^+ Conc, N	Stainless Steel[a] Solubility, g/liter		
	From Fe Determination	From Ni Determination	Avg.
4.46	88.8	84.2	86.5
4.8	77.8	81.2	79.5
5.3	71.3	74.9	73.1
5.7	75.6	80.0	77.8
5.7	72.0	77.9	75.0
5.95	77.5	80.2	78.8
6.1	72.0	78.9	75.4
6.15	--	72.4	72.4
7.8	64.8	71.2	68.0
8.6	64.5	67.4	66.0
8.7	--	65.6	65.6
9.1	58.5	66.8	62.6
9.4	60.9	64.3	62.6
9.45	62.2	62.5	62.3
9.5	56.5	56.2	56.3
10.0	45.1	46.0	45.6
10.1	41.6	43.7	42.6
15.1	12.4	12.9	12.6

[a]69.0% Fe, 9.73% Ni, 17.9% Cr by analysis.

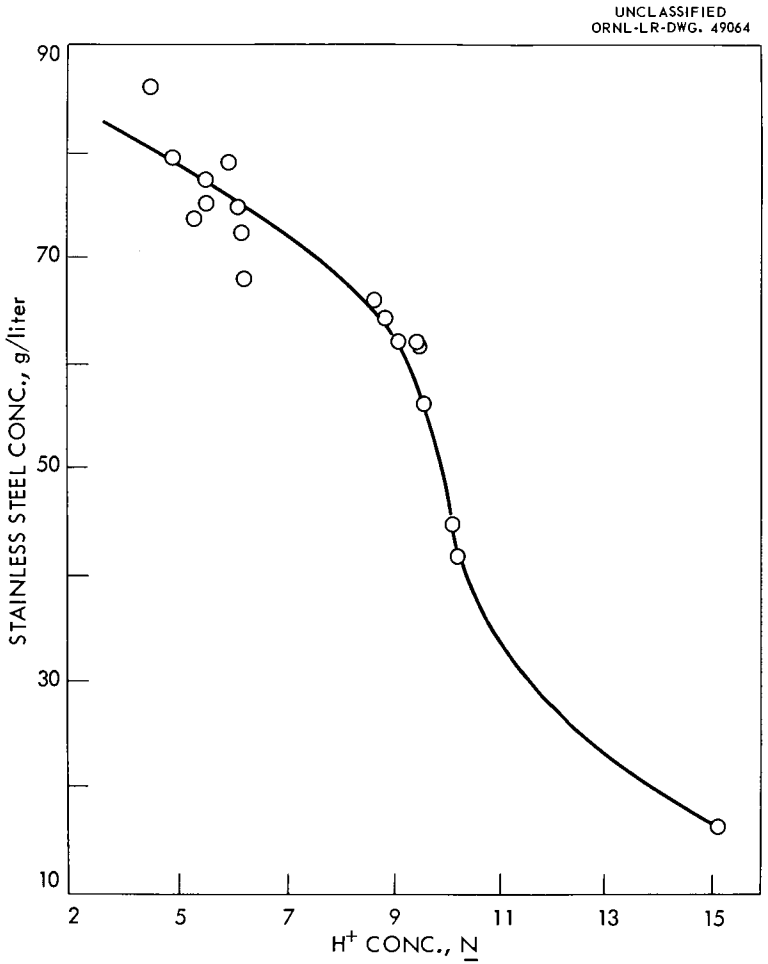

Fig. 3. Solubility of stainless steel in sulfuric acid at 25°C. Stainless steel composition: 69% Fe, 17.9% Cr, 9.73% Ni.

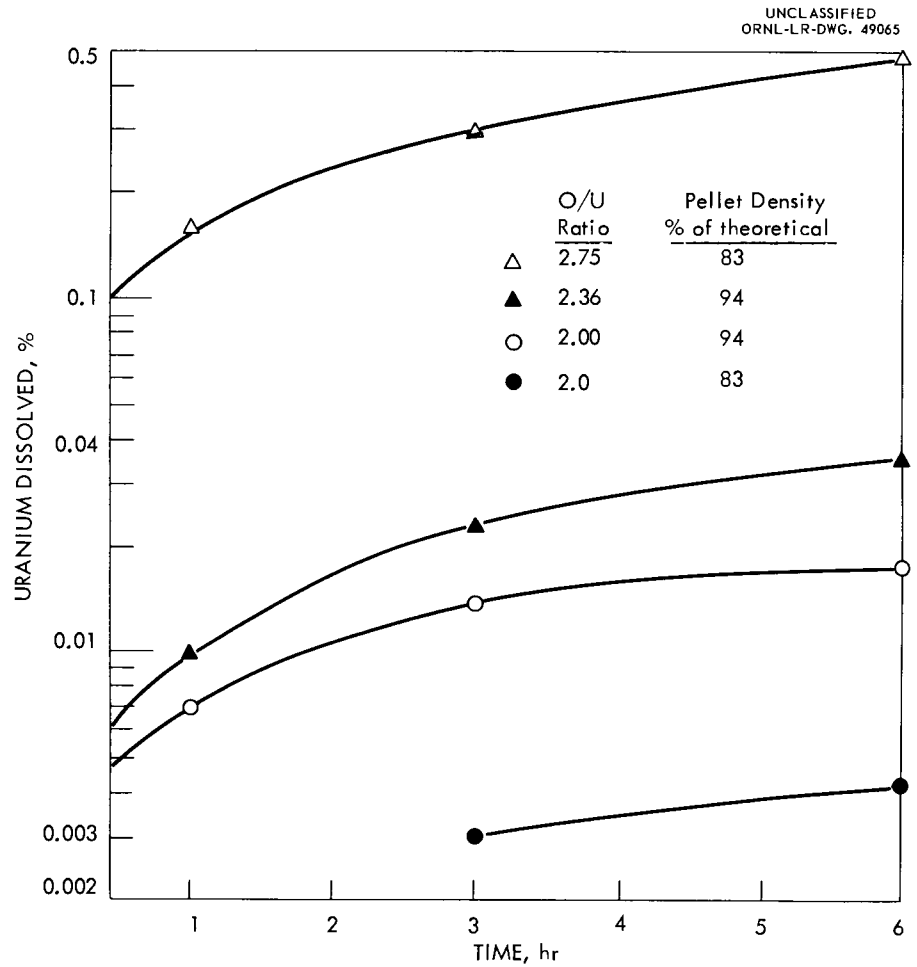

Fig. 4. Effect of O/U ratio and pellet density on uranium losses from 95% ThO_2-5% UO_2 pellets exposed to boiling 6 M H_2SO_4. 5 ml of acid per gram of pellets.

Data were obtained from solutions produced by dissolving 304L stainless steel in sulfuric acid rather than by direct equilibration of the solid sulfates with various acid solutions. Direct equilibration could lead to problems if the solid sulfates did not enter the solution in the ratio in which they exist in the steel. To obtain approximate solubility data by the dissolution technique, pieces of 304L stainless steel (69.0% Fe, 17.9% Cr, 9.73% Ni) were dissolved in boiling sulfuric acid varying in initial concentration from 6 to 16 N. Samples of the solution were withdrawn at frequent intervals (usually 1-2 min) and allowed to cool to room temperature. In solutions where the room temperature solubility had been exceeded during the dissolution, precipitation occurred. By careful visual inspection, it was possible to determine the last sample taken which was cooled to room temperature without precipitation occurring. The stainless steel concentration in this solution was very close to the solubility limit. Since precipitation had not occurred, the iron, nickel, and chromium were present in solution in the same ratio in which they existed in the steel.

3.2 Variables Affecting Uranium Losses During Sulfex Decladding

3.2.1 Pellet Density and O/U Ratio. With pellets in which the O/U ratio was 2.00, the amount of uranium lost to boiling 6 M H_2SO_4 in 24 hr was less than 0.1% and appeared to be independent of pellet density between 83 and 94% of theoretical (Fig. 4). In these and subsequent experiments described in this section, whole pellets were contacted with decladding reagents at a ratio of acid volume to pellet weight of 5 ml/g. The uranium loss was a function of the O/U ratio, particularly with pellets whose density was about 83% of theoretical. For example, uranium losses in 6 hr contact with boiling 6 M H_2SO_4 were 0.004 and 0.5% when the O/U ratios were 2.00 and 2.75, respectively (Fig. 4). The loss in 6 hr was less than 0.04% with pellets of low O/U ratio and/or densities greater than 90% of theoretical. Since losses are even lower to actual decladding solutions,[10] i.e., those containing dissolved stainless steel, it is anticipated that losses in processing of actual Consolidated Edison fuel would be less than 0.1% since the fuel pellets will be about 93% of theoretical density and the O/U ratio will probably be 2.01 or less.[1,11]

3.2.2 Particle Size. While experimental data are somewhat contradictory,[1] it is anticipated that some cracking of the fuel pellets will occur during reactor operation. The results of experiments with high-density fuel classified according to mesh size show that losses in 10 hr probably will be less than 0.5% with either dilute aqua regia or sulfuric acid if the fuel particles are larger than 100 mesh (Fig. 5a and b). The rate of dissolution increases with decreasing particle size so that losses will be high if large quantities of fines are produced during irradiation. Comparison of the lower curves in Fig. 5a and b (which are replotted as the lower curves in Fig. 6) shows that the rate of solution of high-density pellets is about the same with either decladding reagent. However, the rate of uranium dissolution is higher in final Darex solutions than in initial due to the presence of dissolved stainless steel.[10] The pellets used in this series of experiments were 95.8% ThO_2—4.2% $UO_{2.36}$ and had a density 94% of theoretical.

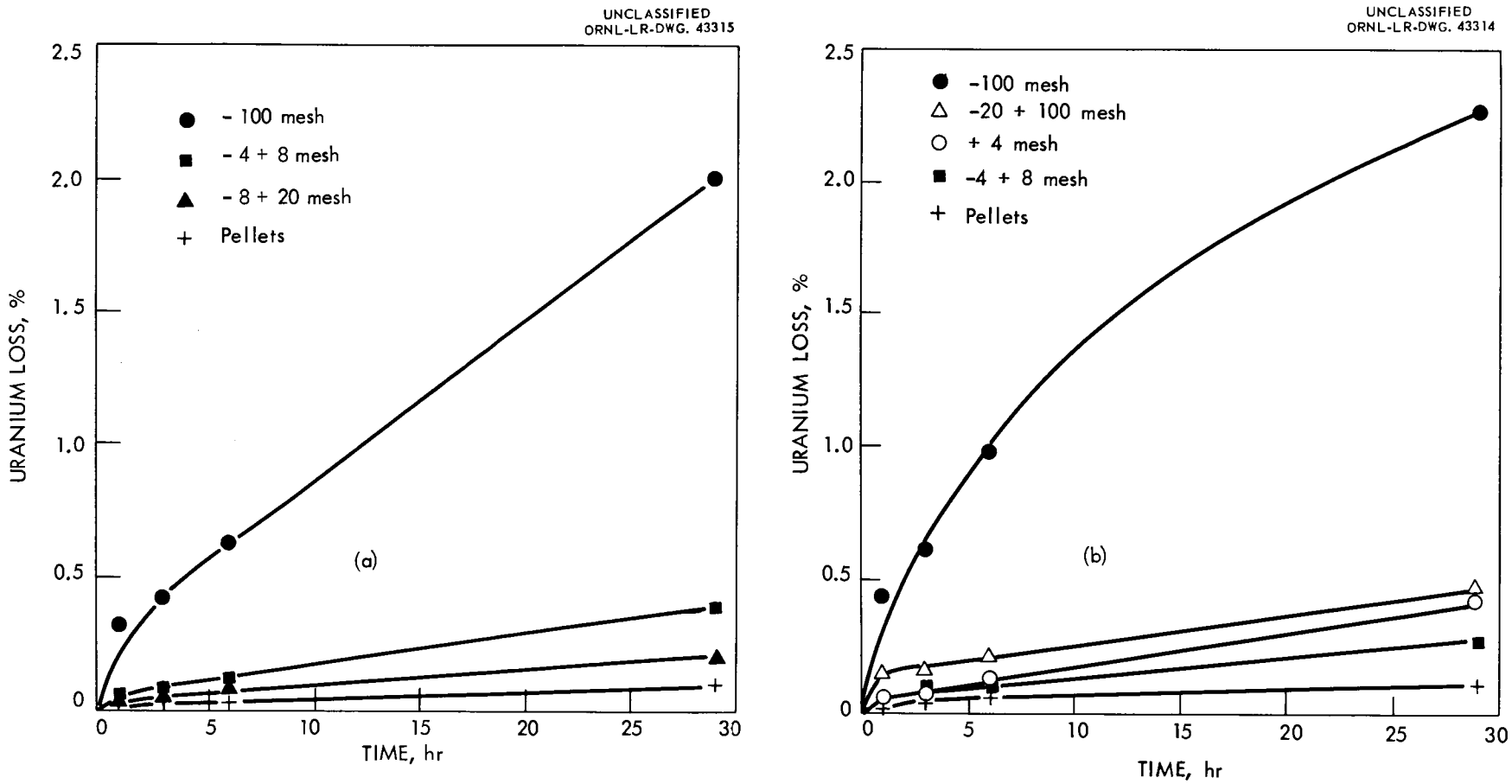

Fig. 5. Uranium losses from thorium oxide—uranium oxide fuel to boiling (a) 6 M H_2SO_4 and (b) 5 M HNO_3—2 M HCl as a function of mesh size and time. Pellets 95.8% ThO_2, 4.2% $UO_{2.36}$; 94% of theoretical density. 50 ml of acid used per 5-g sample.

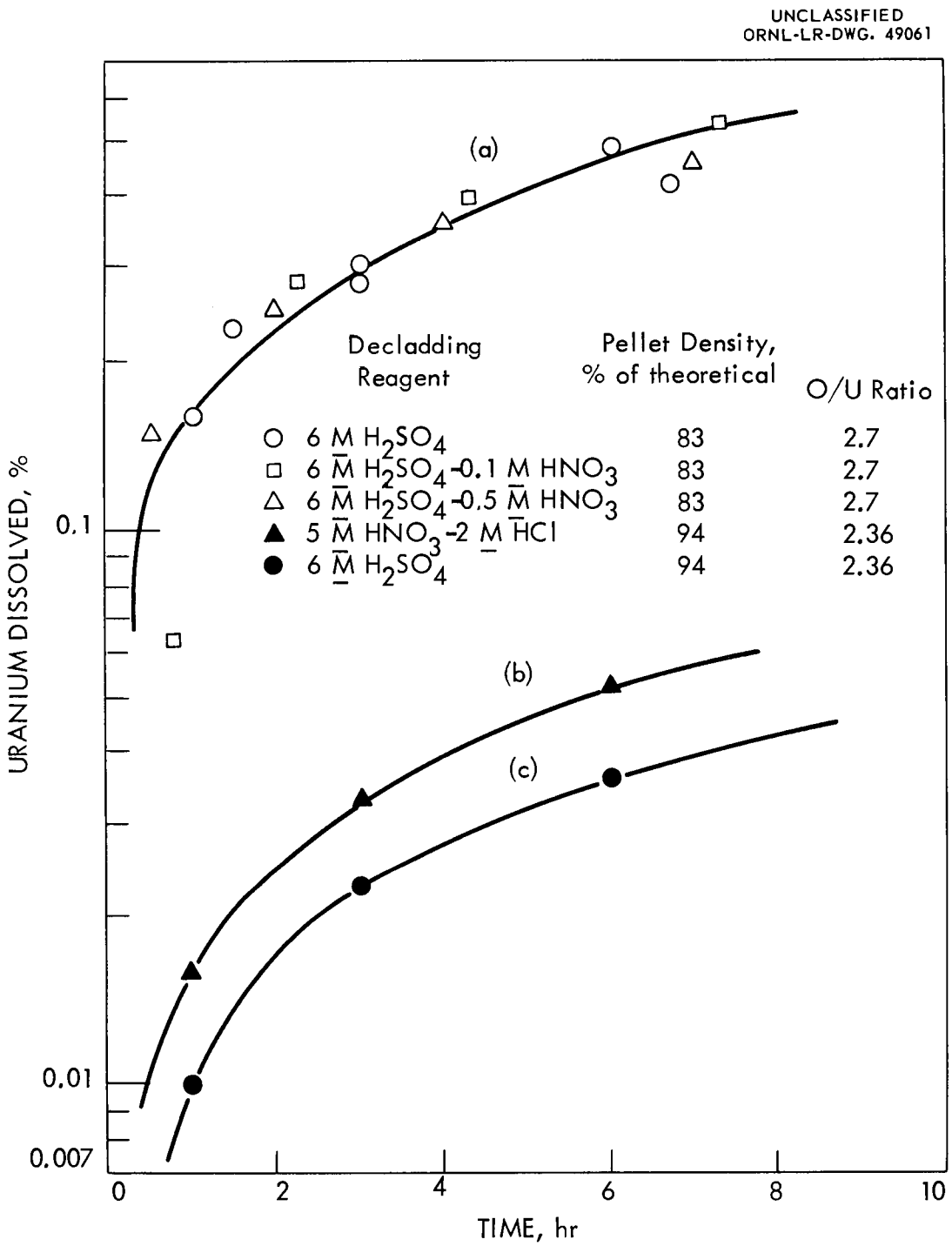

Fig. 6. Uranium losses from (a) 95% ThO_2-5% UO_2 fuel pellets and (b,c) 95.8% ThO_2-4.2% UO_2 as a function of time and pellet density in various decladding solutions.

3.2.3 Cross-contamination of Solutions. Since the Darex reagent contains 5 M HNO_3, its contamination by traces of concentrated nitric acid from the core dissolvent would not lead to higher fuel losses during decladding. Similarly with sulfuric acid solutions, the presence of up to 0.5 M HNO_3 in boiling 6 M H_2SO_4 had no effect on the rate at which uranium was dissolved from 95% ThO_2—5% $UO_{2.7}$ pellets whose density was about 83% of theoretical (Fig. 6, curve a). Because of the role of nitrate in causing passivation, the sulfuric acid will probably be treated with formic acid[7] or some other equally effective reagent to destroy any nitrate present.

3.3 Variables Affecting Rate of Core Dissolution

3.3.1 Nitric Acid Concentration. The most efficient dissolvent for thorium and thorium oxide which is compatible with common materials of construction and the TBP-nitric acid solvent extraction processes which have been developed is concentrated nitric acid containing a trace of fluoride. Earlier studies have shown that the optimum fluoride concentration is about 0.04 M[12] and that the reaction rate is at its maximum when the nitric acid concentration is about 13 M.[13] Data reported here confirm previous findings[13] that the initial (10-min) rate increases with increasing acid concentration (Fig. 7a). The 10-min rate also appeared to increase with acid excess up to 400% (Fig. 7b); however, if the reaction rate measured was truly an initial rate, it should depend only on the acid concentration and not on the excess. The apparent changes in rate with increasing acid excess probably reflect the effect on the rate of the different thorium concentrations attained during the 10-min tests. Why the rate passes through a maximum at about 400% excess is not readily apparent. While the general effect of acid concentration was the same for all pellets, the actual rates depended on other variables such as pellet density and particle size; e.g., the maximum rates shown in Figs. 7a and 7b reflect the difference in density of the pellets used. All pellets used in these and subsequent studies were about 1.28 cm long with a diameter of about 0.66 cm.

3.3.2 Aluminum Concentration. Aluminum nitrate will be required in the core dissolvent in concentrations up to 0.1 M to prevent excessive corrosion of both titanium and Ni-o-nel.[5] While the effect is not great, the initial (10-min) rate of dissolution of fuel pellets decreased with increasing aluminum concentration. For example, the initial (10-min) rate of dissolution of 96% ThO_2—3.6% $UO_{2.7}$—0.4% CaF_2 pellets (81% of theoretical density) in 200% excess of boiling 13 M HNO_3-0.04 M NaF decreased from 9 to 4.7 mg $min^{-1}cm^{-2}$ as the aluminum concentration in the dissolvent increased from 0 to 0.4 M (Fig. 8). Complete dissolution of the pellets containing fluoride to produce a solution 1 M in thorium would increase the fluoride concentration by only 0.02 M. Release of fluoride from the pellets would, therefore, have no effect in a 10-min test. In the Sulfex-Thorex process, where a Ni-o-nel vessel is to be used, the aluminum concentration in the dissolvent will be about 0.1 M, which will decrease the rate 20%. With the Darex titanium dissolver, 0.04 M will afford sufficient protection.

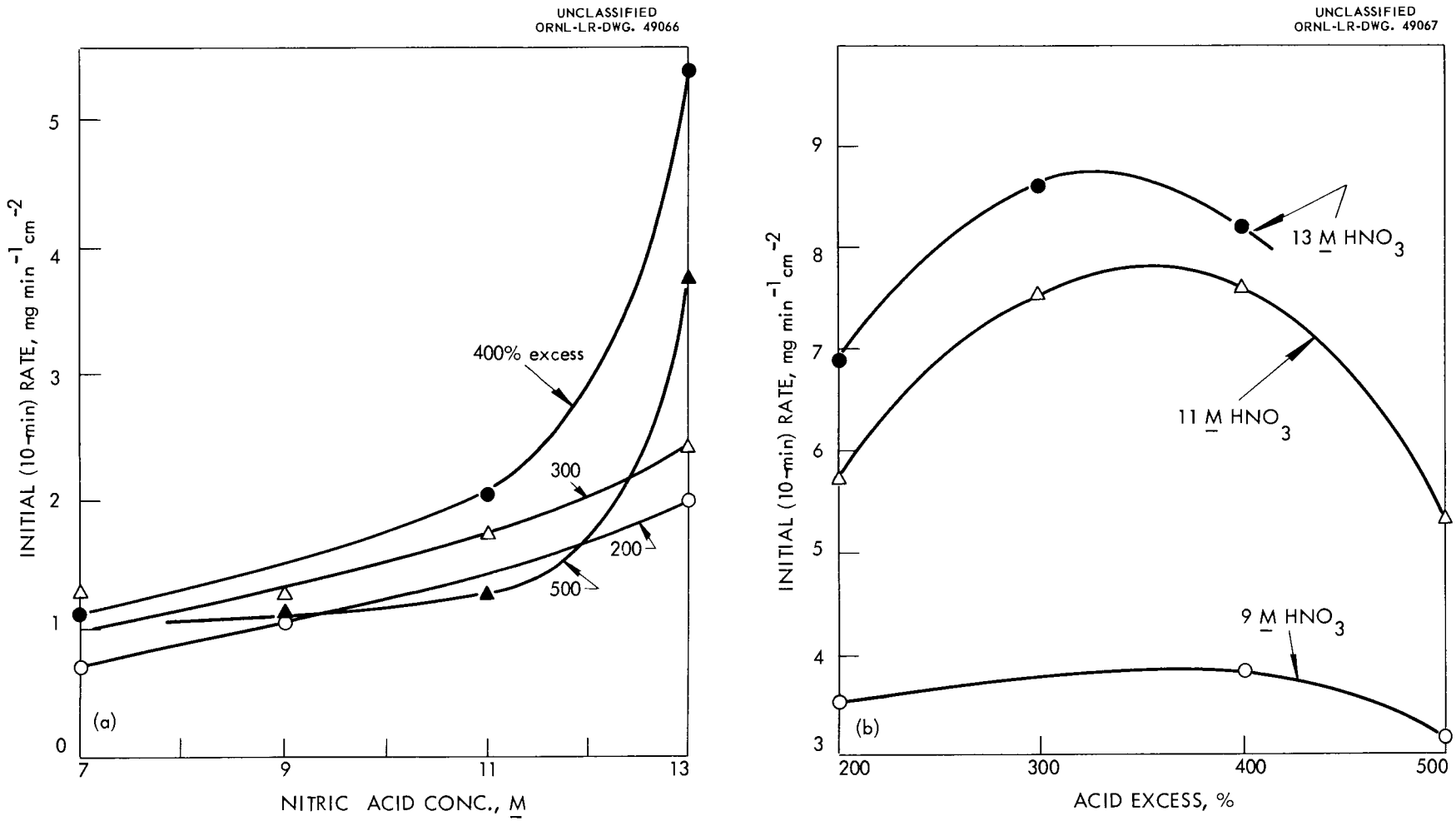

Fig. 7. Effect of acid concentration and excess on the initial (10-min) rate of dissolution of thorium oxide-uranium oxide pellets in boiling nitric acid containing 0.04 M NaF and 0.1 M $Al(NO_3)_3$. (a) pellets, 95.6% ThO_2-4.4% $UO_{2.03}$, 84% of theoretical density; (b) pellets, 95.8% ThO_2-4.2% $UO_{2.36}$, 94% of theoretical density.

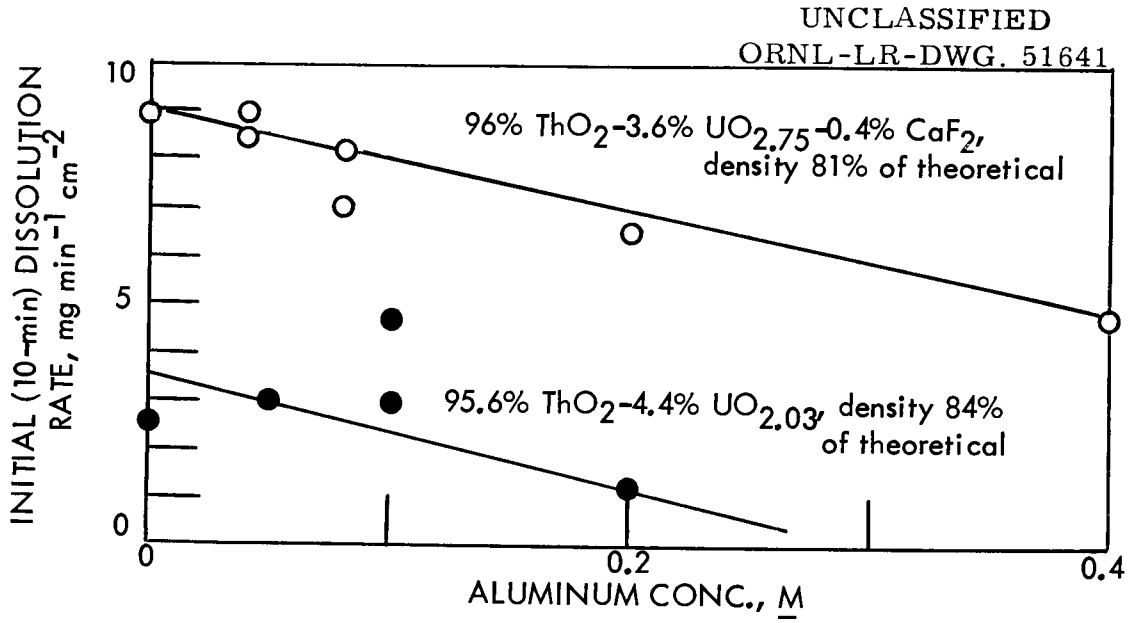

Fig. 8. Effect of aluminum concentration on the initial (10-min) rate of dissolution of thorium oxide-uranium oxide pellets in 200% excess of boiling 13 M HNO_3-0.04 M NaF.

3.3.3 Pellet Density and O/U Ratio. The variable having the greatest effect on the rate of dissolution of thorium oxide fuel pellets in 13 M HNO_3—0.04 M NaF was the density of the pellets. A plot of all data obtained with 200% excess of boiling 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$ as dissolvent shows that the initial (10-min) rate of dissolution of 95% ThO_2-5% UO_2 pellets decreases from about 16 to 2 mg $min^{-1}cm^{-2}$ as the pellet density increases from 60 to 94% of theoretical (Fig. 9a). Anomalous results were obtained with a few pellets, but generally the rate was dependent only on the density, the O/U ratio having virtually no effect on the rate. The time required for total dissolution generally increased from about 3 to 20 hr as the pellet density increased from 60 to 90% of theoretical (Fig. 9b).

From the data obtained it appears that specification grade Consolidated Edison fuel pellets (93% of theoretical density; O/U ratio of 2.01 or less) will be very difficult to dissolve completely in less than 25 hr in boiling 13 M HNO_3—0.04 M NaF. There is also a high probability that very refractive residues will be formed since the temperature inside the fuel pellets can get as high as 2500°C.[1] On the other hand, if the pellets shatter during irradiation, the increased surface area would aid in the dissolution (Sect. 3.3.4).

3.3.4 Particle Size. As shown qualitatively in earlier studies,[3,13] the rate of dissolution of sintered ThO_2-UO_2 fuel in HNO_3-NaF solutions increased markedly when the fuel was powdered. The amount of fuel (originally 95.8% ThO_2—4.2% $UO_{2.36}$, 94% of theoretical density) dissolved in 5 hr in

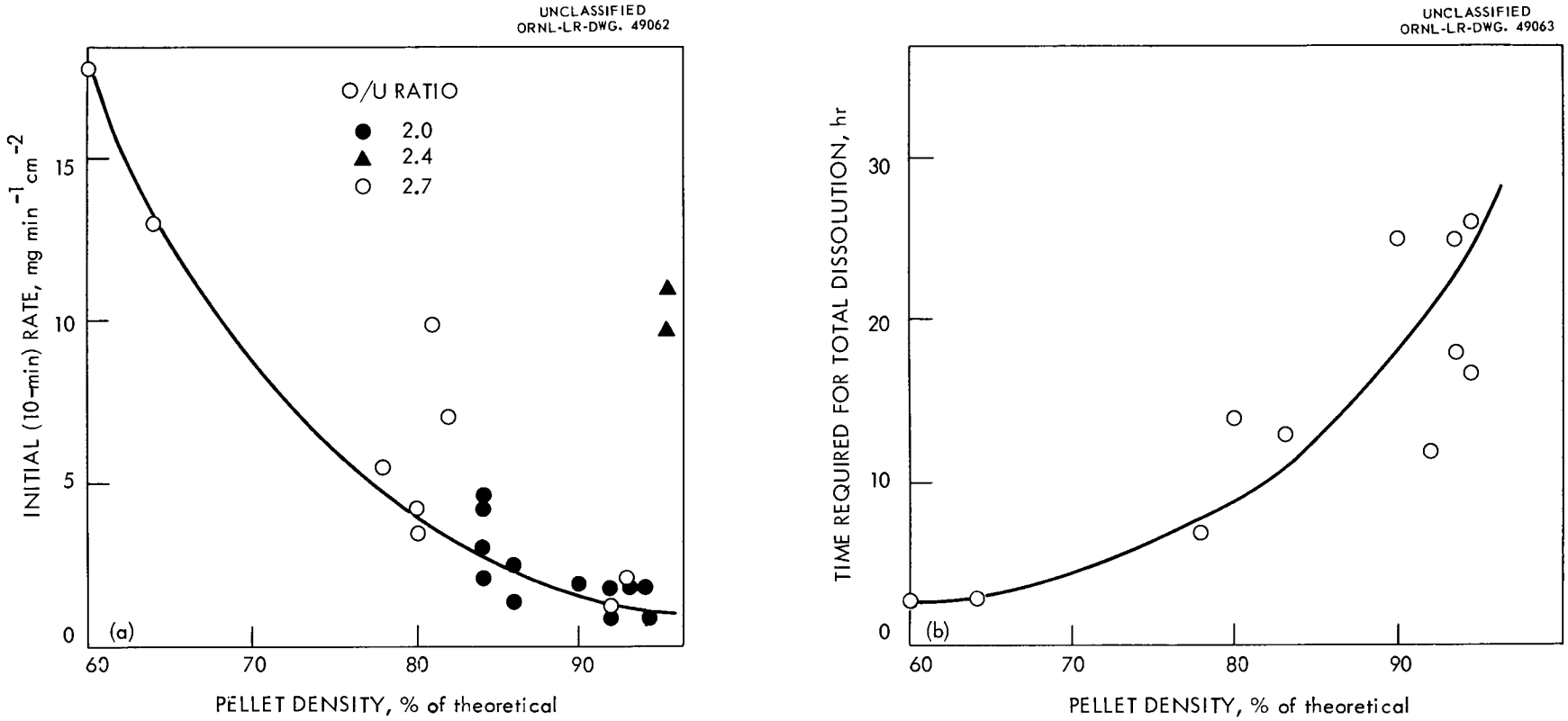

Fig. 9. Effect of pellet density on (a) initial (10-min) rate of dissolution and (b) total dissolution time for 95% ThO_2-5% UO_2 pellets in 200% excess of boiling 13 M HNO_3 - 0.04 M NaF-0.1 M $Al(NO_3)_3$.

200% excess of boiling 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$ increased from about 72 to 99% as the particle size decreased from whole pellets to -100 mesh particles (Fig. 10). Grinding of the fuel pellets prior to dissolution might ensure complete dissolution in a reasonable time but would be difficult to accomplish.

3.3.5 Iron Concentration. In quest of a new dissolvent for sintered ThO_2 it was discovered that the addition of ferric nitrate to nitric acid increased the rate of reaction. With 95.8% ThO_2—4.2% $UO_{2.36}$ pellets (94% of theoretical density) the initial (10-min) rate of dissolution in 200% excess of boiling 13 M HNO_3—0.04 M NaF was maximum, about 9.0 mg $min^{-1}cm^{-2}$, when the $Fe(NO_3)_3$ concentration was 0.5 M (Fig. 11).

These results suggest a total dissolution method in which the stainless steel is dissolved in dilute aqua regia and the chloride removed before concentrated nitric acid and the fluoride catalyst are added to dissolve the fuel pellets.[6] The chloride must be removed prior to addition of the fluoride to prevent excessive corrosion of the dissolver. An analogous process based on dissolution of the stainless steel in sulfuric acid is completely unfeasible because of the insolubility of thorium oxide in nitric acid-sulfuric acid mixtures (Sect. 3.3.6). A major disadvantage of the total dissolution process is the large volume of high-activity solvent extraction raffinate waste generated because of the inclusion of stainless steel in the solvent extraction feed solution.

3.3.6 Sulfate Concentration. The presence of sulfate ion in the core dissolvent decreased the rate of dissolution. In two series of experiments in which 96% ThO_2—4% UO_2 pellets were dissolved in 200% excess of boiling 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$ the initial (10-min) rate of reaction was decreased by a factor of about 5.5 as the sulfate concentration in the dissolvent increased from 0 to 0.1 M (Fig. 12). Even with 0.5 M Fe^{3+} in the dissolvent, the rate was decreased by the same factor. The diminution in reaction rate in the presence of sulfate appears to be due to the formation of an insoluble film of thorium sulfate[14] on the surface of the pellets. Washing of the pellets with dilute acid or soaking in cold water[15] prior to introduction of the dissolvent removed most of the sulfate. It is clear, however, that careful washing will be required after a Sulfex decladding step so that the problems associated with the core dissolution are not magnified.

3.3.7 Fluoride Concentration. With 95.8% ThO_2—4.2% $UO_{2.36}$ pellets (94% of theoretical density), the initial (10-min) rate of dissolution in 200% excess of boiling 13 M HNO_3 was maximum when the fluoride concentration was 0.06-0.07 M (Fig. 13). These results agree generally with those obtained at HAPO[12] in studies of the dissolution of thorium metal. It appears that the fluoride concentration in the dissolvent could be increased to 0.06 M if corrosion of the dissolver did not become excessive. Fluoride concentrations higher than 0.07 M are undesirable because ThF_4 is precipitated,[13] a fact which probably accounts for the lower rates at the higher fluoride concentrations.

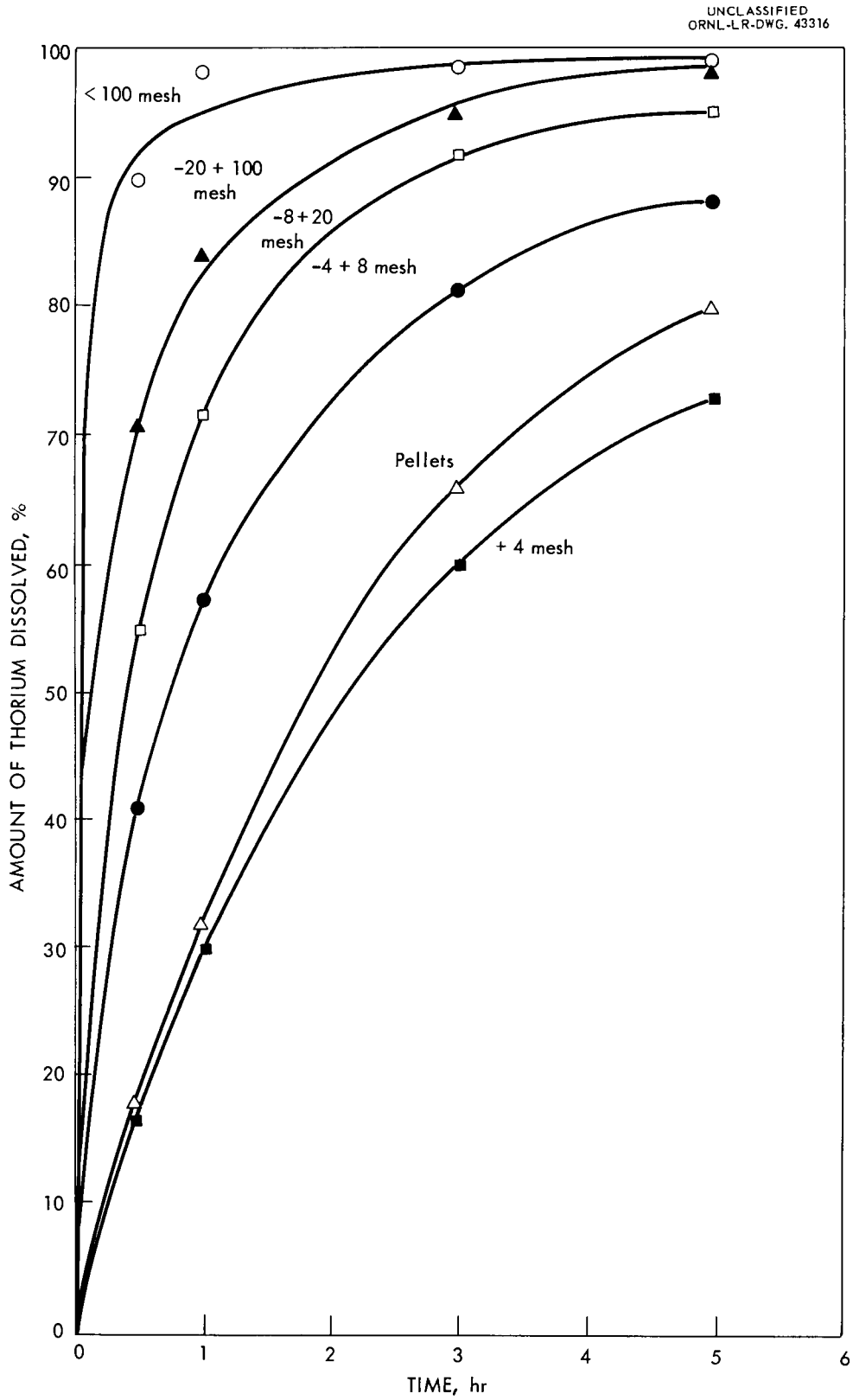

Fig. 10. Effect of particle size on the dissolution of 95.8% ThO_2-$UO_{2.36}$ fuel in a 200% excess of boiling 13 M HNO_3-0.04 M NaF-0.1 M $Al(NO_3)_3$. Pellets were 94% of theoretical.

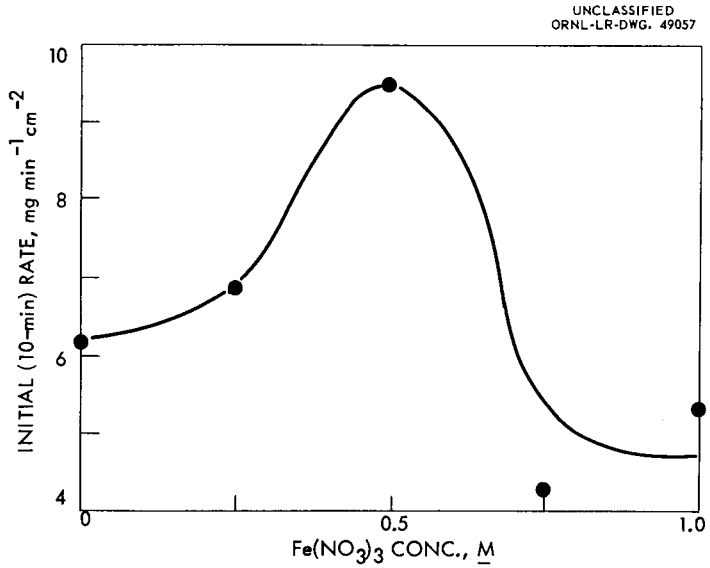

Fig. 11. Effect of ferric nitrate concentration on dissolution of 95.8% ThO_2-4.2% $UO_{2.36}$ pellets (94% of theoretical density) in 200% excess of boiling 13 M HNO_3-0.04 M NaF.

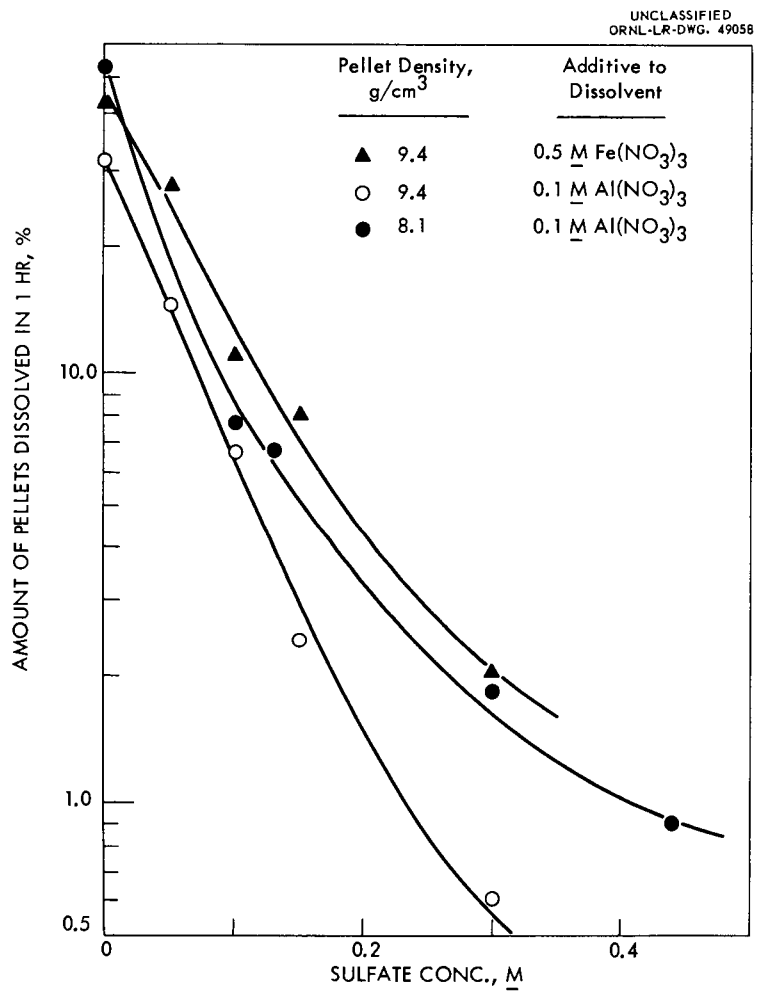

Fig. 12. Effect of sulfate concentration on dissolution of 96% thorium oxide-4% uranium oxide pellets in 200% excess of boiling 13 M HNO_3-0.04 M NaF containing either iron or aluminum.

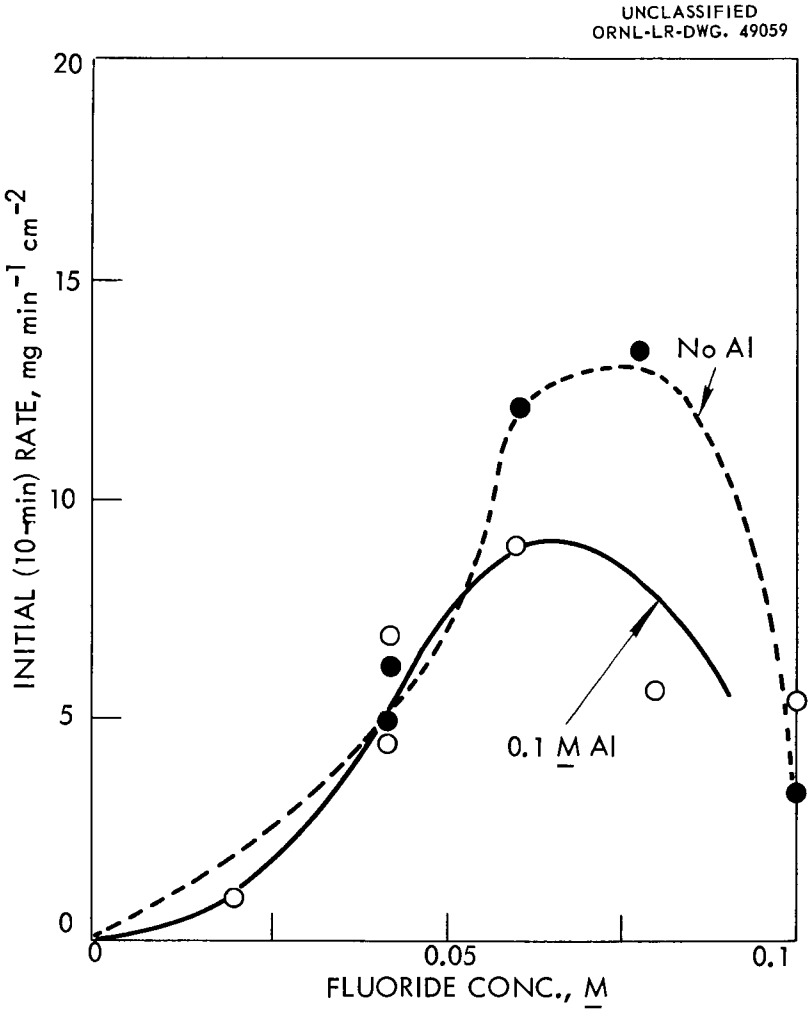

Fig. 13. Effect of fluoride concentration on the rate of dissolution of 95.8% ThO_2-$UO_{2.36}$ pellets (94% of theoretical density) in 200% excess of boiling 13 M HNO_3.

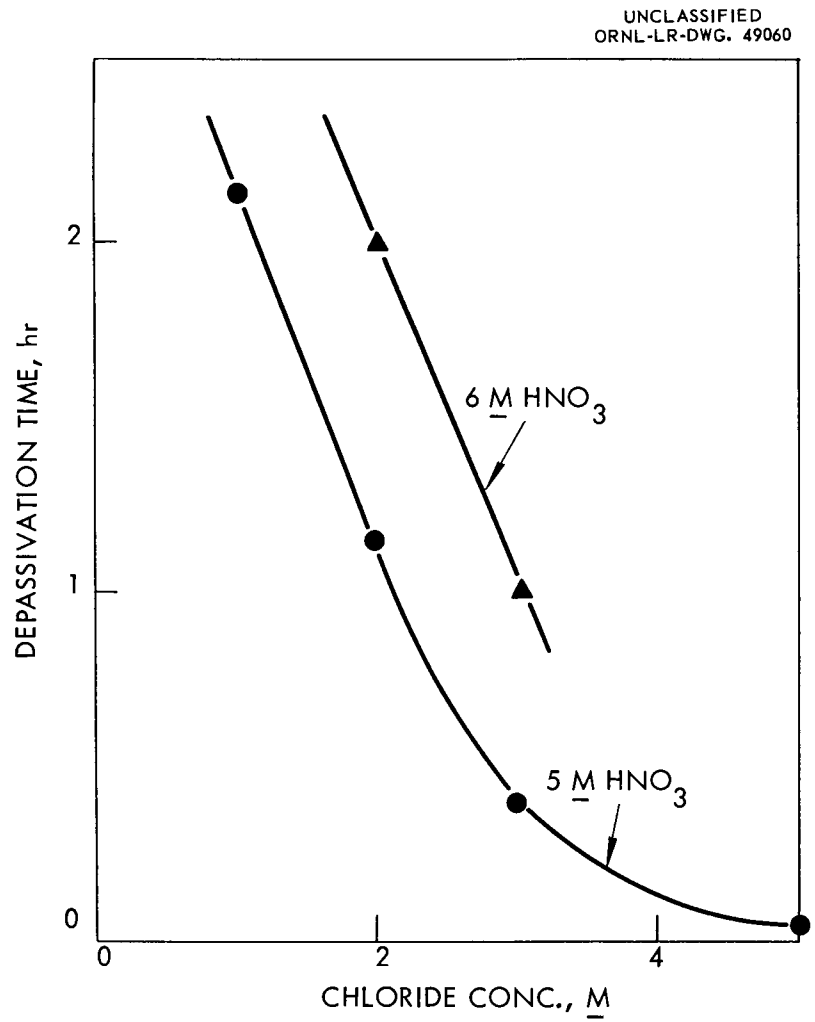

Fig. 14. Effect of chloride concentration on depassivation of 304L stainless steel in dilute aqua regia. Specimens in contact with titanium. Passivation treatment: Reflux 1 hr in 15 M HNO_3-0.3 M CrO_3.

3.4 Flowsheet Demonstration Experiments

3.4.1 Darex-Thorex Flowsheet. Three series of flowsheet demonstration experiments were performed following basically the Darex-Thorex flowsheet shown in Fig. 1. In two series the decladding reagent was 5 M HNO_3—2 M HCl; in the third, 1 M HNO_3—2 M HCl was used. All experiments were conducted with 6-in.-long 5/16-in.-dia simulated unirradiated Consolidated Edison fuel pins containing about 44 g of 95% ThO_2—UO_2 pellets and about 25 g of 304L stainless steel (25 mils thick). Two types of pellets were used, one about 81% and the other about 94% of theoretical density. With either decladding reagent, uranium losses were 0.1-0.5% and 0.05%, respectively (Table 2). These results are precisely those expected from studies with pellets alone (Sect. 3.2.1). In addition, losses from the pellets of lower density were in excellent agreement with those obtained in a series of cyclic dissolution experiments with the same type of fuel pin.[2] Use of 1 M HNO_3—2 M HCl as the decladding reagent offered no advantages over the usual reagent, 5 M HNO_3—2 M HCl.

The rate of dissolution of 304 stainless steel in boiling 5 M HNO_3 containing HCl is at its maximum of about 60 mg $min^{-1}cm^{-2}$ when the HCl concentration is 2 M; the rate decreases abruptly to about 35 mg $min^{-1}cm^{-2}$ as the HCl concentration is increased above 2 M.[6] As anticipated, the rate of dissolution of the stainless steel decreased when the nitric acid concentration in the dissolvent was lowered.[6] With 5 M HNO_3—2 M HCl, dissolution of the 30-mil tubing and the solid (1/4 in. dia by 1/2 in. long) stainless steel end plugs was complete in about 1 hr, yielding a solution containing 55 g of stainless steel per liter.

About 95% of the core pellets dissolved during the first, 5-hr, contact with 200% excess of boiling 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$ when their density was only 81% of theoretical (Table 3). With pellets whose density was 94% of theoretical, only about 75% dissolved in the first digestion. In a second, 3-hr, digestion with 1/3 volume of fresh dissolvent, dissolution of the lower density pellets was essentially complete whereas 1-4% of the higher density pellets remained after a second, 5-hr, digestion with a full volume of fresh dissolvent. With the higher density pellets dissolution was not complete even after a third, 3- to 5-hr, digestion with 1/3 volume of fresh dissolvent.

3.4.2 Sulfex-Thorex Flowsheet. In nine flowsheet demonstrations of the Sulfex-Thorex process, uranium losses during decladding with boiling 6 M H_2SO_4 were proportional to the density of the fuel pellets. Generally losses were between 0.1 and 0.5% with pellets of density 81% of theoretical and were always less than 0.04% when the pellet density was 94% of theoretical (Table 4). In all runs the decladding reaction was initiated with boiling 6 M H_2SO_4; however, 300% excess was used in two experiments instead of the usual 200% and in another two experiments the solution was diluted to 4 M sulfate shortly after the reaction began.

Table 2. Decladding of Simulated, Unirradiated Consolidated Edison Fuel Pins[a] by the Darex Process

Run No.	Decladding Reagent[b]	Decladding Time, hr	SS Dissolved, %	Pellet Density,[c] g/cm^3	Pellet O/U Ratio	Losses, % U	Losses, % Th
DCE-3	5 M HNO_3—2 M HCl	0.5	97.3	8.1	2.75	0.41	0.014
DCE-4	5 M HNO_3—2 M HCl	0.75	100	8.1	2.75	0.34	0.006
DCE-1	5 M HNO_3—2 M HCl	1.0	100	8.1	2.75	0.42	0.043
DCE-6	5 M HNO_3—2 M HCl	1.0	100	9.4	2.36	0.026	0.003
DCE-2	5 M HNO_3—2 M HCl	2.0	100	8.1	2.75	0.29	0.019
Avg. of cyclic runs,[ref 2]	5 M HNO_3—2 M HCl	3.0	100	8.1	2.75	0.27	—
DCE-7	5 M HNO_3—2 M HCl	4.0	100	9.4	2.36	0.050	0.004
DCE-5	1 M HNO_3—2 M HCl	1.0	77.2	8.1	2.75	0.16	0.035
DCE-8	1 M HNO_3—2 M HCl	1.0	69	9.4	2.36	0.001	0.006
DCE-9	1 M HNO_3—2 M HCl	4.0	83	9.4	2.36	0.001	0.005

[a]Pins were ~6 in. long and contained 25 g of stainless steel and 44 g of pellets.
[b]Stainless steel concentration in undiluted waste solution was 55 g/liter.
[c]Theoretical density about 10 g/cm^3.

Table 3. Dissolution of 95% ThO_2-5% UO_2 Core Pellets After Decladding Simulated, Unirradiated Consolidated Edison Fuel Pins[a] by the Darex Process

First digestion: 200% excess of boiling 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$, 5 hr
Second digestion: 1/3 vol of fresh dissolvent, 3 hr

Run No.	Pellet Density, % of theoretical	Core Dissolved, % 1st Digestion	Core Dissolved, % 2nd Digestion	Core Undissolved after Two Digestions, %
DCE-3	81	—	—	0.55[b]
DCE-4	81	94.6	4.7	0.69[b]
DCE-1	81	100[c]	—	—
DCE-6	94	69.2	27.0[c]	3.80
DCE-2	81	95.5	4.3	0.22[b]
Avg. of cyclic runs,[ref 2]	81	94.1	5.9	0
DCE-7	94	81.6	17.4[d]	1.0
DCE-5	81	97.1	2.7	0.16[b]
DCE-8	94	73.2	24.3[d]	2.5
DCE-9	94	78.0	19.1[d]	2.9

[a]Pins were ~6 in. long and contained 25 g of stainless steel and 44 g of pellets.
[b]Heel was mostly Kaowool which was present as end plug in fuel pin.
[c]Single 21-hr digestion.
[d]Second digestion, equal volume of fresh dissolvent.

Table 4. Decladding of Simulated Unirradiated Consolidated Edison Fuel Pins[a] by the Sulfex Process

Run No.	Reagent	Acid Excess, %	Pellet Density,[b] g/cm^3	Pellet O/U Ratio	Decladding Time, hr	SS Dissolved, %	Losses, % U	Losses, % Th
AI	6 M H_2SO_4	200	8.1	2.75	5	80	0.18	0.054
HF-1	6 M H_2SO_4	200	9.4	2.36	1	77.1	0.010	0.003
HF-2	6 M H_2SO_4	200	9.4	2.36	5	91.0	0.038	0.005
HF-5	6 M H_2SO_4	200	9.4	2.36	5	86.8	0.038	0.010
HF-3D	6 M H_2SO_4 diluted to 4 M $SO_4^=$	200	9.4	2.36	3.3	97.7	--	--
HF-5D	6 M H_2SO_4 diluted to 4 M $SO_4^=$	200	9.4	2.36	5	100	0.038	0.006
Avg. of cyclic runs, ref. 2	6 M H_2SO_4 diluted to 4 M $SO_4^=$	200	8.1	2.75	3	82.8	0.36	--
4I	6 M H_2SO_4	300	8.1	2.75	5	100	0.41	0.086
4II	6 M H_2SO_4	300	8.1	2.75	5	100	0.34	0.22
HF-F2	6 M H_2SO_4-- 0.1 M HCOOH	200	9.4	2.36	2	82.8	0.024	0.016

[a]Pins were ~6 in. long and contained 25 g of stainless steel and 44 g of pellets.
[b]Theoretical density about 10 g/cm^3.

The rate of dissolution of the stainless steel was much lower than in dilute aqua regia. For example, in 5 hr, 80-90% of the stainless steel dissolved in 200% excess of boiling 6 M H_2SO_4 whereas dissolution was complete in about 1 hr in 5 M HNO_3—2 M HCl. Waste solutions in each case contained about 50 g of stainless steel per liter. Diluting the Sulfex decladding solution to 4 M sulfate or increasing the acid excess to 300% resulted in a higher rate of reaction (Table 4). Addition of 0.1 M HCOOH, which might be present in the decladding solution to remove nitrate, had no effect on the losses.

Dissolution of the core pellets was generally less complete than if aqua regia had been used as the decladding reagent. In the first, 5-hr, digestion with 200% excess of dissolvent, about 60% of the pellets dissolved compared to about 70% in the Darex-Thorex experiments (Table 5). Lower rates obtained after Sulfex decladding were attributed to contamination of the core dissolvent with sulfate (Sect. 3.3.6).

Table 5. Dissolution of 95% ThO_2-5% UO_2 Core Pellets after Decladding of Simulated Unirradiated Consolidated Edison Fuel Pins[a] by the Sulfex Process

First digestion: boiling 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$, 5 hr
Second digestion: 67% excess of fresh dissolvent based on original wt of pellets, 3 hr

Run No.	Pellet Density, % of theoretical	Acid Excess in 1st Digestion, %	Core Dissolved, % 1st Digestion	Core Dissolved, % 2nd Digestion	Core Undissolved After Two Digestions, %
AI	81	200	93.3	6.6	0.1
HF-1	94	200	58.6	22.3	19.1
HF-2	94	400	77.5	16.1	6.4
HF-5	94	-	-	-	-
HF-3D	94	200	67.7	21.3	11.0
HF-5D	94	200	80.8	16.1	3.1
Avg. of cyclic runs, ref. 2	81	200	77.1	20.7	2.2
4I	81	800	99.7	0.3	0
4II	81	500	96.3	3.6	~0.1
HF-F2	94	200	62.6	19.3	18.1

[a]Pins were ~6 in. long and contained 25 g of stainless steel and 44 g of pellets.

3.5 Passivation Studies

3.5.1 Sulfex Process. Passivation of stainless steel in boiling sulfuric acid can occur under a variety of conditions. This subject has been the object of several previous investigations[3,7,9] and will not be considered further here.

3.5.2 Darex Process. Passivation of stainless steel in dilute aqua regia has been observed previously, but was generally thought to occur only when the chloride concentration in the dissolvent became lower than 1.5 M.[16] In these experiments, however, passivation of stainless steel in contact with titanium occurred in boiling 5 M HNO_3—2 M HCl. It was concluded that the primary cause of the passivation was the fact that the area of the titanium container (a 30-mesh basket, 5 in. high, 1 in. o.d.) was much greater than that of the stainless steel although passivation could also be induced in the absence of titanium by pretreatment of the stainless steel surface (see below). Since passivation could be a serious deterrent to the use of the Darex process, some of the variables affecting passivation of stainless steel in dilute aqua regia were studied.

Small coupons of 304 stainless steel, with surface areas of about 7.7 cm^2, were treated for 1 hr in boiling 15 M HNO_3—0.3 M Cr(VI) to produce an oxidized surface. The time required for active dissolution of the stainless steel to begin, i.e., the depassivation time, in contact with a 30-mesh titanium basket decreased in boiling 5 M HNO_3 from 2 to essentially zero hours as the HCl concentration increased from 1 to 5 M (Fig. 14). At each chloride concentration, the depassivation time was increased by a factor of nearly 2 by increasing the nitric acid concentration to 6 M.

Depassivation times were nearly as long in the absence of titanium; for example, in boiling 5 M HNO_3—2 M HCl the presence of the titanium basket (in otherwise glass equipment) increased the depassivation time only from about 50 to 70 min. Preheating of the acid decreased the depassivation time to about 30 min. Passivation was not encountered with brazed (Nicrobraze 50) specimens or when the aqua regia solution contained 0.04 M NaF.

It is tentatively concluded that if passivation occurs in plant operation, it can easily be broken by adding more HCl to the usual Darex dissolvent, 5 M HNO_3—2 M HCl. No increase in the corrosion rate of titanium would be expected, and the rate of dissolution of the stainless steel would probably be lowered. In practice, some reduction in rate may be desirable to permit easier control of the decladding reaction.

3.6 Off-Gases

3.6.1 Sulfex Process. Dissolution of stainless steel in sulfuric acid proceeds according to the following reactions yielding hydrogen as the only gaseous product:[3]

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

$$Ni + H_2SO_4 \longrightarrow NiSO_4 + H_2$$

$$Cr + 3/2\ H_2SO_4 \longrightarrow 1/2\ Cr_2(SO_4)_3 + 3/2\ H_2$$

In plant operation the hydrogen, after rare gas removal, will either be diluted below the explosive limit or converted to water before discharge to the atmosphere.[17]

3.6.2 Darex Process. As expected, the gases evolved during Darex dissolution vary in composition as the reaction proceeds.[16] The gas will be mainly NO, N_2O, and NO_2 with traces of NOCl, H_2, and Cl_2. For example, less than 0.2% hydrogen was found in the gases evolved during dissolution of 304 stainless steel under flowsheet conditions. With an appropriate system, much of the gas can be reclaimed. Since reactions between hydrogen and several of the nitrogen oxides can be explosive,[18] a thorough study of the gases evolved during dissolution has been initiated.

4.0 REFERENCES

1. J. C. Deddens, Babcock and Wilcox Company, seminar presented before the ORNL Chemical Technology Division, Jan. 26, 1960.

2. L. M. Ferris, "Decladding of Consolidated Edison Power Reactor Fuel by Sulfex and Darex Processes: Cyclic Dissolution Experiments," ORNL-2822 (Jan. 13, 1960).

3. L. M. Ferris and A. H. Kibbey, "Laboratory Development of the Sulfex Process for the Dissolution of Consolidated Edison Power Reactor Fuel," ORNL-2714 (Oct. 16, 1959).

4. W. E. Clark, "Corrosion Status: Sulfex-Thorex (Ni-o-nel) and Darex-Thorex (Titanium) as of June 12, 1959," ORNL-CF-59-6-110. See also C. L. Peterson, P. D. Miller, J. D. Jackson, and F. W. Fink, "Construction Materials for Various Head-end Processes for the Reprocessing of Spent Fuel Elements," BMI-1375 (Aug. 28, 1959).

5. R. H. Rainey, ORNL, personal communication, Jan. 15, 1960.

6. R. E. Blanco, L. M. Ferris, J. R. Flanary, F. G. Kitts, R. H. Rainey, and J. T. Roberts, "Chemical Processing of Power and Research Reactor Fuels at Oak Ridge National Laboratory," in Proc. of AEC Symposium for Chemical Processing of Irradiated Fuels from Power, Test, and Research Reactors," TID-7583 (January 1960), p. 234.

7. T. A. Gens, "Sulfex Process: Depassivation of Stainless Steel," ORNL-2785 (Nov. 6, 1959).

8. W. E. Clark, ORNL, personal communication, Jan. 11, 1960.

9. M. E. Brennan et al., "Fuel Recovery Process for the SIR Mark A," KAPL-933 (July 17, 1953).

10. T. A. Gens, ORNL, personal communication, March 28, 1960.

11. E. J. Silk, Babcock and Wilcox Company, personal communication to J. P. Nichols, ORNL, Feb. 4, 1960.

12. C. A. Goodall, J. L. Hepworth, R. L. Moore, and R. A. Watts, Jr., "A Kinetic Study of the Fluoride-catalyzed Nitric Acid Dissolution of Thorium Metal," HW-40250 (Nov. 17, 1955).

13. W. D. Bond, "Dissolution of Sintered Thorium-Uranium Oxide Fuel in Nitric Acid-Fluoride Solutions," ORNL-2519 (Oct. 28, 1958).

14. Koppel and Holtcamp, Z. anorg. Chem., 69: 274 (1910).

15. R. A. Ewing, Battelle Memorial Institute, personal communication to L. M. Ferris, ORNL (Jan. 25, 1960).

16. W. E. Clark, J. R. Flanary, and F. G. Kitts, "The Darex Process: The Treatment of Stainless Steel Reactor Fuels with Dilute Aqua Regia," ORNL-2712, (in preparation).

17. J. M. Holmes, A. R. Irvine, and J. P. Nichols, ORNL, memo to H. E. Goeller, "Proposed Hydrogen Safety and Disposal Procedures for the PRFR Pilot Plant," Jan. 20, 1960.

18. K. S. Warren, "A Survey of Potential Vapor-phase Explosions in Darex and Sulfex Processes," ORNL-2937 (in preparation).

ORNL-2934
UC-80 Reactors-General
TID-4500 (15th ed.)

INTERNAL DISTRIBUTION

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

EXTERNAL DISTRIBUTION

89-94. Hanford Operations Office (1 copy each to L. P. Bupp, J. T. Christy, V. R. Cooper, M. K. Harmon, O. F. Hill, and C. A. Rohrman)
95-97. Atomic Energy Commission, Washington (1 copy each to F. R. Dowling, E. L. Anderson, and J. A. Lieberman)
98-99. General Atomics (1 copy each to R. F. Benenati and K. G. Steyer)
100-101. Battelle Memorial Institute (R. A. Ewing)
102-103. Atomics International (1 copy each to B. R. Hayward and H. Pearlman)
104. Stanford Research Institute (E. M. Kinderman)

105-109. Hanford Operations Office (1 copy each to K. K. Kennedy, D. M. Paige, C. M. Slansky, J. A. McBride, and F. M. Warzel)
110. Argonne National Laboratory (S. Lawroski)
111. duPont Company, Aiken (J. W. Morris)
112. Radiation Applications, Inc. (H. Shon)
113. Dow Chemical Company (R. J. Teitel)
114. duPont Company, Wilmington (V. R. Thayer)
115. Atomic Energy Commission, Oak Ridge (J. Vanderryn)
116-699. Given distribution as shown in TID-4500 (15th ed.) under Reactors-General category (75 copies - OTS)
700. Brookhaven National Laboratory (B. Manowitz)
701. Division of Research and Development, AEC, ORO