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LABORATORY DEVELOPMENT OF THE SULFEX PROCESS FOR THE DISSOLUTION OF CONSOLIDATED EDISON POWER REACTOR FUEL

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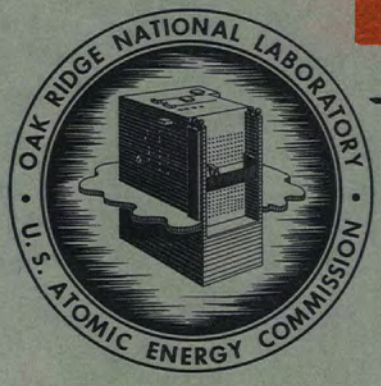

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Chemical Development Section B

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ABSTRACT

Flowsheets given for dissolution of Consolidated Edison power reactor fuel, 96% ThO_2—4% UO_2 sintered pellets clad in type 304L stainless steel, include removal of the stainless steel cladding with a 200% stoichiometric excess of boiling 4 or 6 M H_2SO_4. The ThO_2-UO_2 core is then dissolved in boiling 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$. Essentially complete dissolution of the stainless steel requires about 6 hr in the preferred reagent, 6 M H_2SO_4; only about 80% is dissolved in 6 hr with 4 M H_2SO_4. Uranium and thorium losses to the decladding solution were, in general, less than 0.2 and 0.1%, respectively. After decladding, about 93% of the core is dissolved in 6-7 hr when a 200% stoichiometric excess of dissolvent is used; the resulting solution is 1 M in thorium. The ThO_2-UO_2 heel can be dissolved immediately in about 3 hr in fresh dissolver solution, or can remain through subsequent decladding steps. Aluminum nitrate added to the core dissolver solution to inhibit corrosion does not affect the pellet dissolution rate at concentrations below 0.1 M.

The solubilities of the neutron poisons boron and cadmium in process solutions were determined. Boric acid solubility was 0.2 to 0.4 M in most solutions; that of cadmium was 0.2 to 1.2 M.

CONTENTS

1.0 INTRODUCTION

This report is an interim summary of laboratory work performed in the development of a process for the head-end dissolution of Consolidated Edison power reactor fuel. The Consolidated Edison fuel element will be a type 304 stainless steel tube, 99 in. long, filled with sintered 96% ThO_2—4% UO_2 pellets.[1] According to early reference designs, the end pellets in each tube were to be either Al_2O_3, ZrO_2, or MgO, which would serve as thermal insulators. Early development of a practicable method for reprocessing this fuel is essential since it represents an important class of fuels that will be processed at ORNL on an interim basis. Information obtained in this study will be valuable in devising processing schemes for similar reactor fuels, e.g., the Borax-IV and Rural Cooperative power reactor fuels.[2,3] This report contains the results of preliminary experiments with unirradiated, simulated Consolidated Edison fuel specimens. Most of the experiments were conducted to determine uranium and thorium losses to the decladding solution, the effect of additives (corrosion inhibitors and neutron poisons) on the dissolution rate of cladding and core, and the reproducibility of data when the flowsheets were tested on a laboratory scale.

Much development work on the process remains to be done. Problems of major concern are the passivation of stainless steel in sulfuric acid and the cross-contamination of solutions in the process. Other areas that require major effort include determination of uranium and thorium losses with reactor grade fuel pellets, the effect of radiation on the dissolution processes, finding more suitable dissolution conditions for plant operation, and determination of the solubility of mixed neutron poisons in the process solutions.

Several reagents, including aqua regia[4] and sulfuric acid,[5,7] may be used to dissolve stainless steel. However, dissolution of thorium oxide is most practically achieved in fluoride-catalyzed nitric acid.[8,10] Titanium or tantalum is a suitable container for aqua regia, but resistance of these materials to solutions containing fluoride ion is questionable. Recent experiments, however, show that titanium may be a suitable material of construction for use with nitric acid solutions with low fluoride concentrations. Titanium is rapidly attacked by sulfuric acid. If sulfuric acid is used for the dissolution of the stainless steel cladding, both decladding and core dissolution can be performed in one stainless steel vessel. In this way, the transfer of solid core pellets to another vessel after decladding can be avoided. Hydrogen is the only gas evolved in the dissolution of stainless steel in sulfuric acid. Little off-gas is expected during core dissolution since uranium dioxide is a minor constituent of the fuel. When thorium oxide is dissolved in mixtures of nitric and hydrofluoric acids, the fluoride concentration must be kept below 0.1 M to avoid precipitation of thorium tetrafluoride.[8,9]

The chemical and x-ray analyses for the experiments were provided by the groups of G. R. Wilson, W. R. Laing, and R. L. Sherman of the ORNL Analytical Chemistry Division.

2.0 FLOWSHEETS

Two flowsheets for the first cycle of the head-end dissolution procedure are given in Fig. 1. The difference is in the concentration of the sulfuric acid used for dissolving the stainless steel cladding, which may be 4 or 6 M; 200% stoichiometric excess of boiling acid is used. Six molar H_2SO_4 is preferred. If passivation of the steel is to be avoided, the acid must be boiling[7] before it is admitted to the dissolver. In 6 hr, about 80 and 98% of the stainless steel in the test specimens were dissolved in 4 and 6 M H_2SO_4, respectively. The volume reduction in the refluxing system was approximately 15% with either acid. In the initial stages of the reaction, foaming was severe as a result of the rapid evolution of hydrogen. The uranium lost during decladding was generally less than 0.2%. The solids present after decladding, the ThO_2-UO_2 core pellets and a portion of the stainless steel end caps, are washed with cold water. Approximately 93% of the core material is then dissolved in boiling 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$ in about 6 hr. For core dissolution, a 200% stoichiometric excess of dissolvent is used. The solution resulting from core dissolution, 1 M $Th(NO_3)_4$—8.8 M HNO_3—0.06 M $UO_2(NO_3)_2$, can be adjusted by evaporation of excess acid to conditions suitable for solvent extraction. After each core dissolution, a water wash is necessary to prevent fluoride and nitrate contamination of the next decladding solution.

The heel of ThO_2-UO_2 and stainless steel, which remains after the decladding and first core dissolution steps, may be allowed to increase to a steady-state amount in subsequent cycles, or the ThO_2-UO_2 can be completely dissolved by another contact with fresh dissolver solution before the next decladding step is begun. In the latter case, only the stainless steel end caps would accumulate in subsequent dissolution cycles.

Four molar sulfuric acid was initially chosen as the decladding reagent since, in tests with unirradiated and nonoxidized fuel, it rapidly dissolved the stainless steel cladding and did not present as great a corrosion problem as the 6 M acid. In recent tests with irradiated fuel specimens and autoclaved, unirradiated specimens,[11] the initial rate of dissolution in 4 M H_2SO_4 was very low owing to the passive, oxide-coated surface. It appears, then, that 6 M acid will be required, at least to initiate the reaction, if severe passivation is to be avoided. Since passivation occurs at times in boiling 6 M H_2SO_4 some means for chemical depassivation must be developed to assure uninterrupted operation of a plant.

3.0 RESULTS

3.1 Decladding

Dissolution of Stainless Steels in Sulfuric Acid. About 1.15 moles of hydrogen was evolved when 1 mole (55 g) of an 18-8 stainless steel was dissolved in sulfuric acid. This result is precisely that expected if dissolution occurs according to the reactions

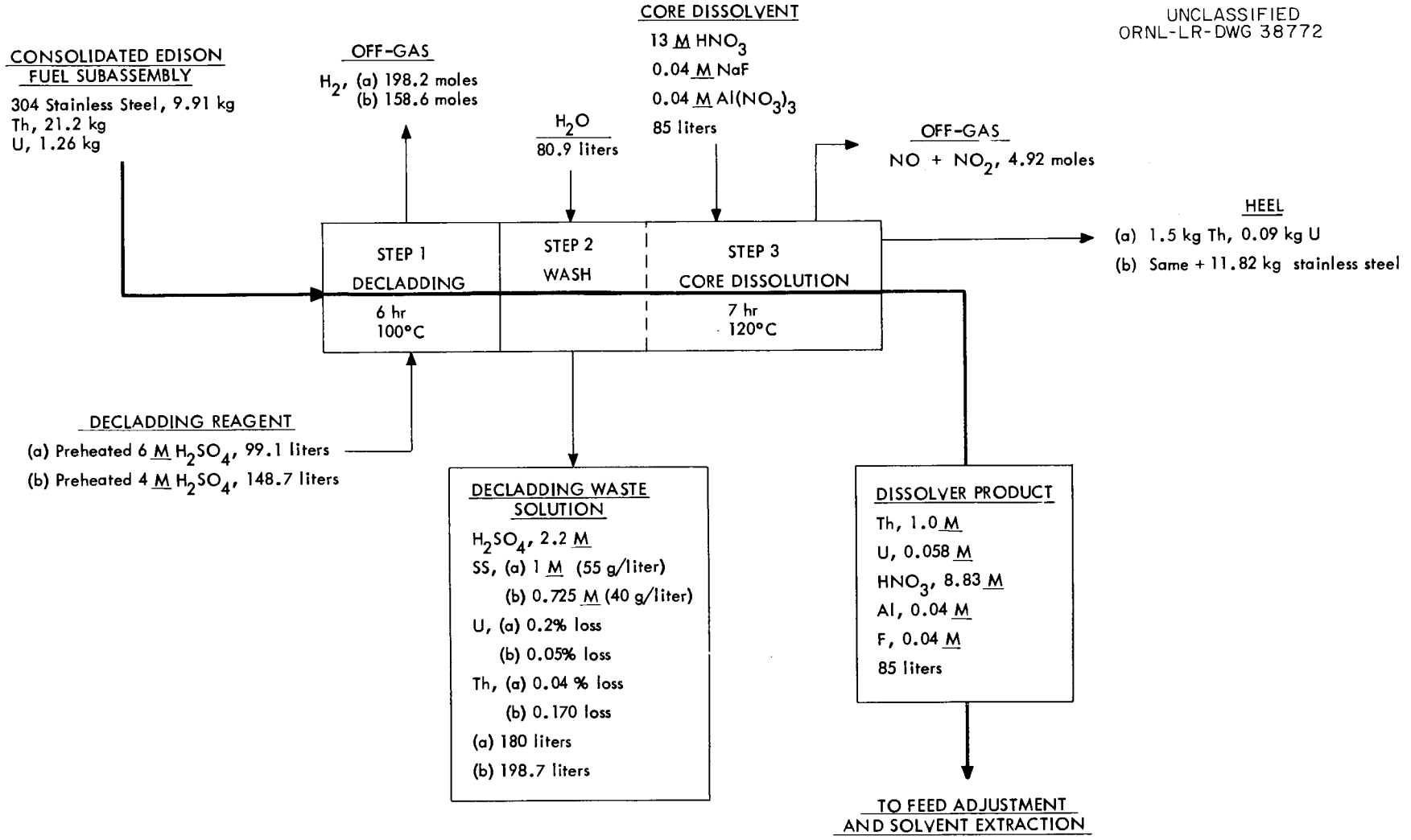

Fig. 1. Flowsheet for dissolution of Consolidated Edison reactor fuel. Decladding achieved with 200% excess of sulfuric acid.

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

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

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

Initial rates of dissolution of various types of stainless steel were determined as a function of acid concentration. The initial rate was acceptably high (> 2 mg/cm^2·min) at concentrations above 3 M H_2SO_4, and was essentially the same for all steels investigated (Fig. 2). Three times the stoichiometric amount of boiling acid was used. Significantly, the presence of 250 ppm boron in 304L stainless steel had no effect on the dissolution rate.

Rates in mg/cm^2·min may be converted to mils/hr by the relation

$$\text{mils/hr} = (\text{mg/min}\cdot\text{cm}^2) \times 2.94.$$

Thus, if an average rate of 5 mg/cm^2·min is maintained, as might be expected with 6 M H_2SO_4, a 30-mil jacket would be removed in about 2 hr.

Effect of Corrosion Inhibitors on the Rate of Dissolution. Since Carpenter 20 and Ni-o-nel alloys are susceptible to corrosion cracking in boiling 6 M H_2SO_4,[12] it was suggested that a small amount of stainless steel sulfates or copper sulfate be present initially to prevent this type of corrosion. In experiments on the initial dissolution rate of stainless steel in 4 and 6 M H_2SO_4 containing varying amounts of these additives, less than 5 g/liter of dissolved stainless steel or copper sulfate was sufficient to cause partial passivation. The initial dissolution rate, as determined by a 5-min. immersion test, was reduced by more than a factor of 250 (Table 1).

Increasing the contact time to 1 hr resulted in even lower average rates (Table 1). However, unirradiated, passivated specimens dissolved in 4 M H_2SO_4 containing 5 g of stainless steel per liter if the specimen was in intimate contact with steel wool. Specimens that had been autoclaved or exposed to air at 300-500°C for a short time, and were completely passive to preheated 6 M H_2SO_4, dissolved in preheated 6 M H_2SO_4 if the passive specimen was in contact with a clean piece of stainless steel or steel wool. The use of sulfuric acid that initially contains dissolved stainless steel as the decladding reagent therefore appears feasible if the initial passivation tendency of the metal can be lowered. Chemical methods for overcoming passivation will be studied since the use of steel wool or other mechanical depassivation techniques may be impractical.

Passivation of stainless steel can also occur if a small amount of nitric acid is present in the sulfuric acid.[5] In boiling 6 M H_2SO_4, type 304L stainless steel became passivated at a nitric acid concentration of 0.015-0.02 M, while in 3 M H_2SO_4, a nitric acid concentration of 0.1 M merely caused a decrease in the rate of dissolution. When the stainless steel specimens were wrapped in steel wool, dissolution was rapid in 3 to 6 M H_2SO_4 even at a nitric acid concentration of 0.2 M.

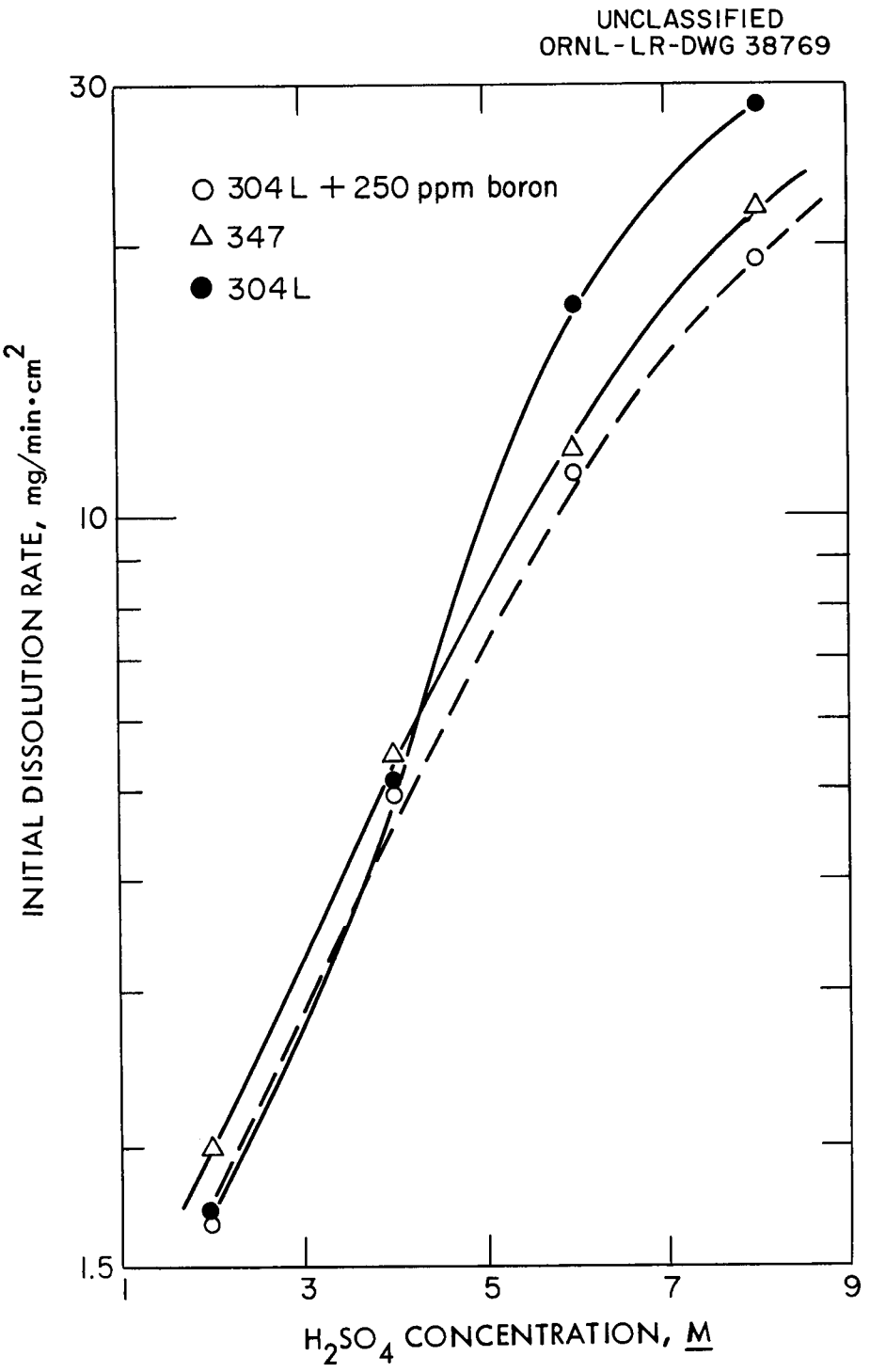

Fig. 2. Initial dissolution rates of stainless steel in boiling sulfuric acid.

Table 1. Dissolution Rates of Stainless Steels in Preheated Sulfuric Acid Containing Dissolved Stainless Steel or Copper Sulfate

Temp at boiling point

Type of Steel	Acid Conc, M	Additive Conc., g/liter	Rate, mg/cm^2·min 5 min Contact	Rate, mg/cm^2·min 1 hr Contact
		Stainless Steel Additive		
304L	4.0	0	5.5	--
		5	0.016	0.0034
		15	0.013	0.0011
		25	0.012	0.0011
	6.0	0	12	--
		5	0.017	0.0019
		15	0.015	0.0013
		25	0.018	0.0018
	4.0	0	4.99	--
		5	0.014	0.0012
		15	0.018	0.0006
		25	0.018	0.0006
	6.0	0	11.3	--
		5	0.028	0.0003
		15	0.021	0.0006
		25	0.014	0.0015
		Copper Additive (as Copper Sulfate)		
304L	4.0	1	0.020	
		5	0.027	
		15	0.024	
	6.0	1	0.011	
		5	0.016	
		15	0.014	
304L containing 250 ppm boron	4.0	1	0.017	
		5	0.016	
		15	0.010	
	6.0	1	0.002	
		5	0.007	
		15	0	

Solubility of Stainless Steel Sulfates in Sulfuric Acid. The solubilities at 25°C of the stainless steel sulfates were determined in solutions obtained by dissolution of stainless steel starting with 100, 200, and 300% stoichiometric excesses of 4 and 6 M H_2SO_4. In each case, samples of the boiling solution were obtained as a function of time, and the approximate stainless steel concentration at which precipitation occurred on cooling to 25°C was determined. With both 4 and 6 M H_2SO_4, the solubility of stainless steel at 25°C in the solutions produced by dissolution of 304L stainless steel in 100 and 200% excesses of these acids was approximately 60 g/liter (Table 2). With 300% excess of either 4 or 6 M H_2SO_4, the stainless steel solubility was only about 35 g/liter. Dissolution conditions can be adjusted so that about 100 g of stainless steel dissolves per liter of boiling solution. Even with 300% excess of either 4 or 6 M H_2SO_4, a 3-fold dilution of the hot dissolver solution results in a clear, stable solution at room temperature. Under any conditions expected in the process, 3-fold dilution of the decladding solution will yield a waste solution free of precipitate. If the decladding procedure is adjusted so that only a small amount of the end caps is dissolved, i.e., only the tubing is removed, the solution resulting from use of 200% excess of acid will contain less than 50 g of stainless steel per liter and will, therefore, not require dilution.

Table 2. Solubility of Stainless Steel in Sulfuric Acid at 25°C

Initial H_2SO_4 Conc., M	Stoichiometric Excess, %	Approximate SS Solubility at 25°C, g/liter	H^+ Conc. in Saturated Solution, M
4.0	100	70	2.0
	200	60	2.67
	300	35	3.0
6.0	100	60	3.0
	200	70	4.0
	300	40	4.50

Dissolution of Brazing Alloy. The fuel rods will be brazed in places to structural supports to assure stability of the fuel assemblies. Nicrobraze-50, which dissolves much more slowly than 304L stainless steel in boiling 6 M H_2SO_4, will probably be used as the brazing alloy. Specimens consisting of three small sections of tubing that had been brazed together were contacted with successive portions of boiling 6 M H_2SO_4. After all the tubing had dissolved, the brazed areas remained. Contacting the brazed areas with fresh 6 M H_2SO_4 for about 6 hr did not noticeably affect them. In all probability, the amount of brazing alloy will increase steadily with each dissolution cycle.

Exposure of ThO_2-UO_2 Pellets to Sulfuric Acid. Exposure of sintered 96% ThO_2—4% UO_2 pellets to boiling 6 M H_2SO_4 for periods of up to 30 hr resulted in uranium losses in excess of 0.5% (Fig. 3a). Recent analyses by H. Kubota

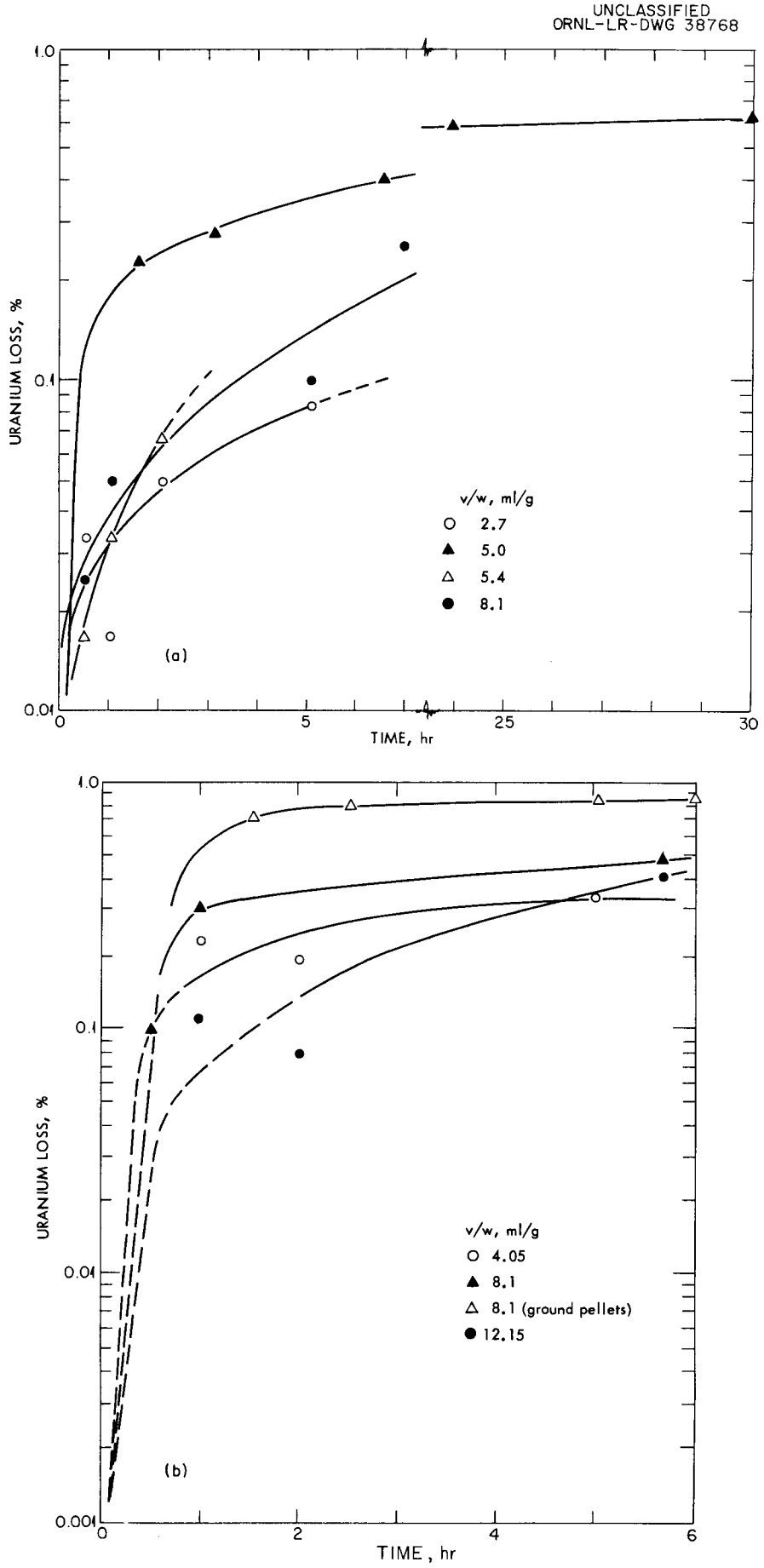

Fig. 3. Effect of volume/weight ratio and time on amount of uranium dissolved from sintered ThO_2-UO_2 pellets by boiling (a) 6 M H_2SO_4 (b) 4 M H_2SO_4.

of the ORNL Analytical Chemistry Division indicate that the uranium in these pellets was probably present as U_3O_8 instead of UO_2; i.e., the O/U atomic ratio was 2.75. Losses from pellets of this type are expected to be higher than from those in which the uranium is present as UO_2. In future experiments, this point will be checked in experiments with hydrogen-fired pellets. The volume-of-acid to weight-of-pellet ratio did not appear to be an important variable. For comparison, it should be noted that under flowsheet conditions this ratio is between 4 and 6. Uranium losses to 4 M H_2SO_4 approached 1% in a short time when the pellets were ground to a powder before digestion (Fig. 3b). On the basis of the flowsheet runs (Sec. 3.6), uranium losses appear to be lower when stainless steel is being dissolved or is present in the sulfuric acid. For example, the uranium loss in flowsheet runs with 4 M H_2SO_4 was generally less than 0.05% in 6 hr compared to about 0.3% in acid containing no dissolved stainless steel. This observation is in agreement with more detailed work at Hanford with pure UO_2.[13]

3.2 Core Dissolution

Effect of Stoichiometric Excess on Dissolution Rate. In a recent study by Bond[9] the rate of dissolution of sintered 96% ThO_2—4% UO_2 pellets in HNO_3-HF solutions was highest when the nitric acid concentration was 13 M. Dissolution proceeded according to the reactions

$$ThO_2 + 4HNO_3 \xrightarrow{F^-} Th(NO_3)_4 + 2H_2O$$

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

Fluoride concentrations up to 0.1 M could be used without fear of ThF_4 precipitation. The initial rate of dissolution was markedly decreased if $Th(NO_3)_4$ was present in the initial dissolver solutions, but increased with increasing acid excess. Dissolution was complete to form solutions containing less than 0.6 M Th in 4-5 hr when the excess was greater than 500% (Fig. 4a). However, at high excesses, the final nitric acid concentration was also high, varying from about 8.5 M with a 200% excess to 11.5 M with a 1300% excess. Complete dissolution with a 200% excess of acid to form a 1.0 M Th solution required 15-20 hr. After about 4 hr, however, the amount dissolved in a 200% excess was about 90% compared to 97% at excesses of 500% or greater. In order to conserve reagents, decrease volumes, and maintain a high metal concentration in the product solution, the conditions selected as optimum are those where the acid excess was about 200%, yielding a final solution which is about 1 M $Th(NO_3)_4$ and 8.5 M HNO_3.

In other scouting experiments fused thoria dissolved somewhat more slowly than the sintered pellets (Fig. 4b), and dissolution of the sintered pellets was complete in about 3 hr in a 200% excess when they were ground to a powder (Fig. 5).

Effect of Aluminum on Dissolution Rate. The corrosiveness of HNO_3-HF solutions can be reduced if aluminum ion is present to complex

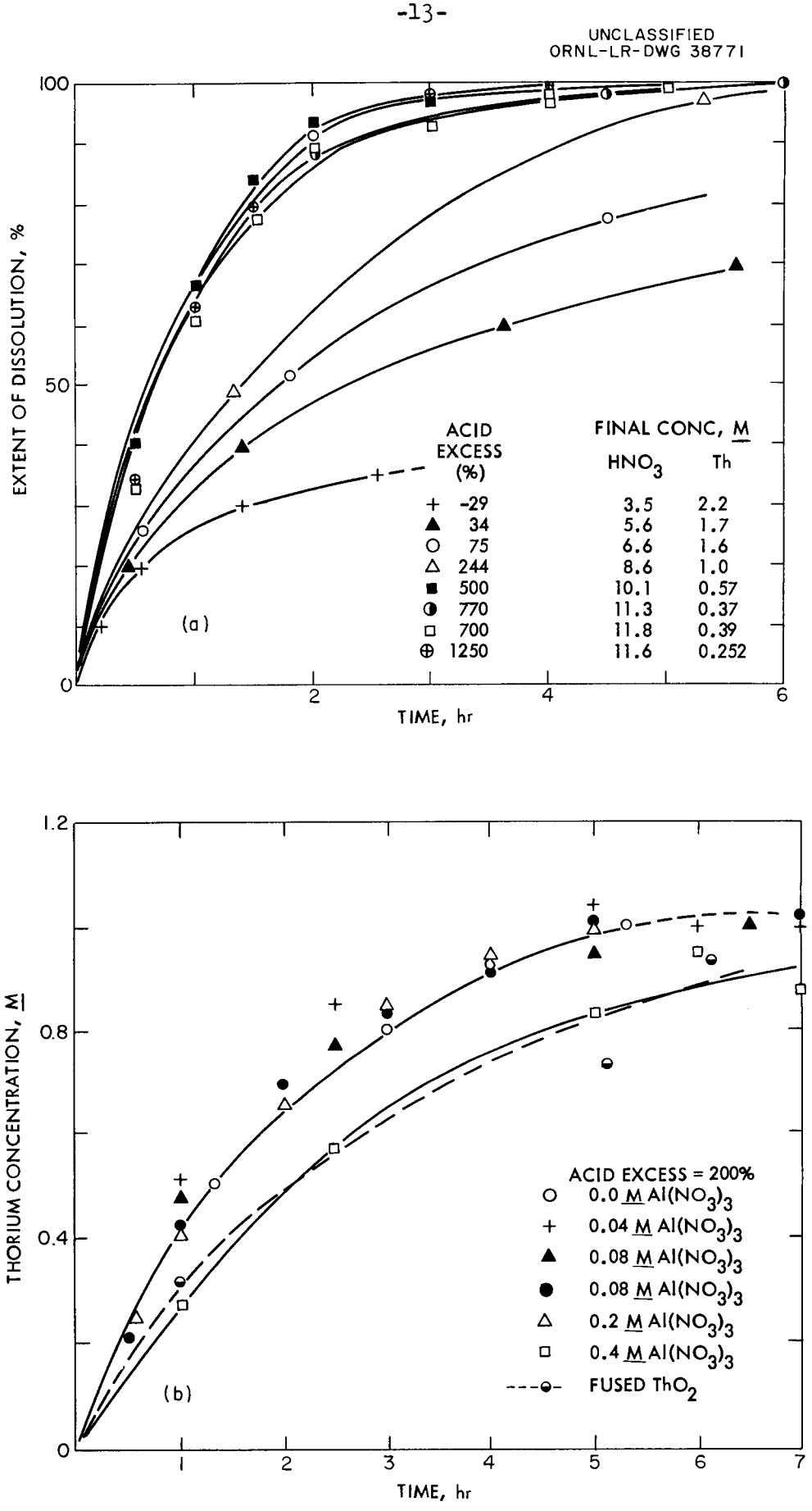

Fig. 4. Effect of (a) acid excess and (b) aluminum concentration on dissolution of sintered 96% ThO_2-4% UO_2 pellets in boiling 13 M HNO_3 - 0.04 M NaF.

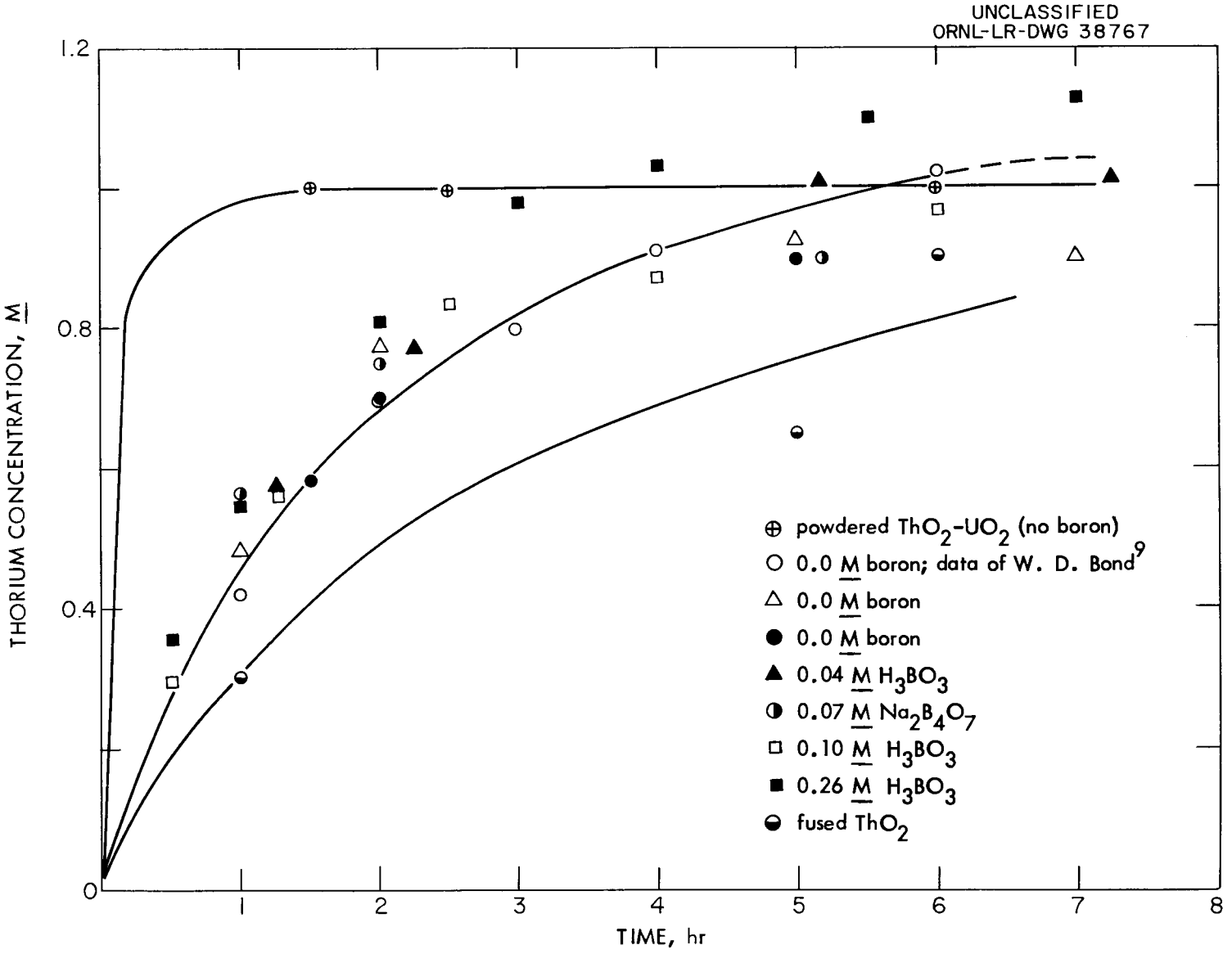

Fig. 5. Dissolution of Sintered ThO_2–UO_2 in Solutions of 13 M HNO_3–0.04 M NaF–0.04 M $Al(NO_3)_3$ Containing Boron. Acid excess = 200%.

fluoride ion. Several experiments were performed to determine the effect of aluminum on the dissolution rate of sintered ThO_2-UO_2* pellets in boiling 13 M HNO_3-0.04 M NaF solutions. In all experiments a 200% excess of acid was used. Aluminum in concentrations of 0.2 M or lower had no effect on the dissolution rate (Fig. 4b). Under these conditions, approximately 93% of the core dissolved in 6-7 hr. At higher aluminum concentrations, the rate was decreased. Recent corrosion tests at Battelle Memorial Institute[14] indicate that the corrosion rates of Ni-o-nel and Carpenter 20 stainless steel are lower in the presence of 0.1 M $Al(NO_3)_3$. According to the data given above, this amount of aluminum should not affect the core dissolution procedure.

Effect of Boron on Dissolution Rate. Several scouting experiments were performed to see if boron, as H_3BO_3 or $Na_2B_4O_7$, had any effect on the rate of core dissolution. Boron may be required in the process solutions as a neutron poison. Boron at concentrations up to 0.26 M, the saturation concentration, had no effect on the rate of dissolution (Fig. 5). About 15% of the boron volatilized during the 7-hr core dissolution.

Effect of Stainless Steel on Core Dissolution. Since in the process it is expected that some stainless steel will be present during core dissolution, the effect of iron concentration on the dissolution rate of ThO_2-UO_2 pellets was briefly investigated. Ferric nitrate in concentrations up to 1 M had no deleterious effect on the dissolution rate. On the contrary, the percentage dissolved in 6-7 hr appeared to be higher when iron was present in solution (Table 4).

Table 4. Effect of Iron Concentration on Dissolution of Sintered ThO_2—UO_2 Pellets in Boiling 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$

Iron Conc., M	Pellets Dissolved in 7 hr, %	
	200% Acid Excess	770% Acid Excess
0	92	100
0.05	99.9	100
0.2	99.9	100
1.0	97.4	100

Boildown Experiment. Since only about 93% of the core is expected to dissolve in one contact with dissolver solution under tentative flowsheet conditions (Fig. 1), the effect of a boildown on the dissolver heel was briefly investigated. The normal 93% of the core was dissolved under reflux in 7 hr under flowsheet conditions. Then, condensation of the vapors was discontinued, and the system was heated to 160°C and

* All pellets used in this study were more nearly ThO_2-U_3O_8 than ThO_2-UO_2 (see p. 12).

maintained there for a short time. Even after this treatment, the total thorium dissolved corresponded to only 96% of the original pellets. Boildown will be required as part of the feed adjustment prior to solvent extraction, but present plans call for its being done in a separate tank.

3.3 Solubilities of Neutron Poisons in Process Solutions

Because of severe criticality problems associated with the proposed flowsheet, it may be necessary to have neutron poisons present in each process solution.[15] The most likely choices are boron, cadmium, and rare earths. In the case of boron the metal concentration must be about equal to the uranium concentration for effective poisoning.

The solubilities at 25°C of H_3BO_3, $Na_2B_4O_7$, $CdSO_4$, and $Cd(NO_3)_2$ in several process solutions were determined.[3] The solubility of H_3BO_3 was 0.2 to 0.4 M in most of the solutions investigated while that of cadmium was somewhat higher (Table 5). Solubilities of the rare earths have not yet been determined.

3.4 Dissolution of Insulating Materials

According to the original concept, each Consolidated Edison fuel tube was to contain, in addition to the fuel pellets, end pellets of some ceramic to serve as thermal insulators.[1] Some of the ceramics considered were Al_2O_3, ZrO_2, and MgO. It is generally conceded that neither Al_2O_3 nor ZrO_2 will dissolve rapidly in the process solutions, and apparently irradiated MgO dissolves slowly in nitric acid.[5] In the proposed process they would be allowed to accumulate through several dissolution cycles. However, eventually these pellets would have to be removed from the system, either chemically or mechanically.

In an attempt to determine the feasibility of chemically dissolving unirradiated specimens of the respective ceramics, rates of dissolution of specimens that had been sintered at 1400°C for 17 hr were determined. Sintered MgO dissolved readily in the core dissolvent, while the other oxides were only slightly attacked in 7 hr by either 6 M H_2SO_4 or the core dissolvent (Fig. 6). From these results it is obvious that MgO is preferred from a chemical standpoint, even if radiation causes a marked reduction in its rate of dissolution. This latter point will be checked in experiments with irradiated MgO.

3.5 Alternative Dissolvents for Clad and Core

Hanford has suggested[19] the use of HF-HNO_3 mixtures instead of sulfuric acid for decladding stainless-steel—oxide fuels. If such solutions prove practicable, it might be possible to dissolve Consolidated Edison fuel *in toto*. Short-term tests in Teflon vessels indicated a prohibitively low rate of dissolution of 304L stainless steel in HF-HNO_3 solutions (Table 6). Furthermore, for complete dissolution of Consolidated Edison fuel, the fluoride concentration in the core dissolver solution must be less than 0.1 M to avoid precipitation of ThF_4. Since the rate of dissolution of stainless steel increases with increasing HF concentration, at least a 50-fold dilution of the decladding solution

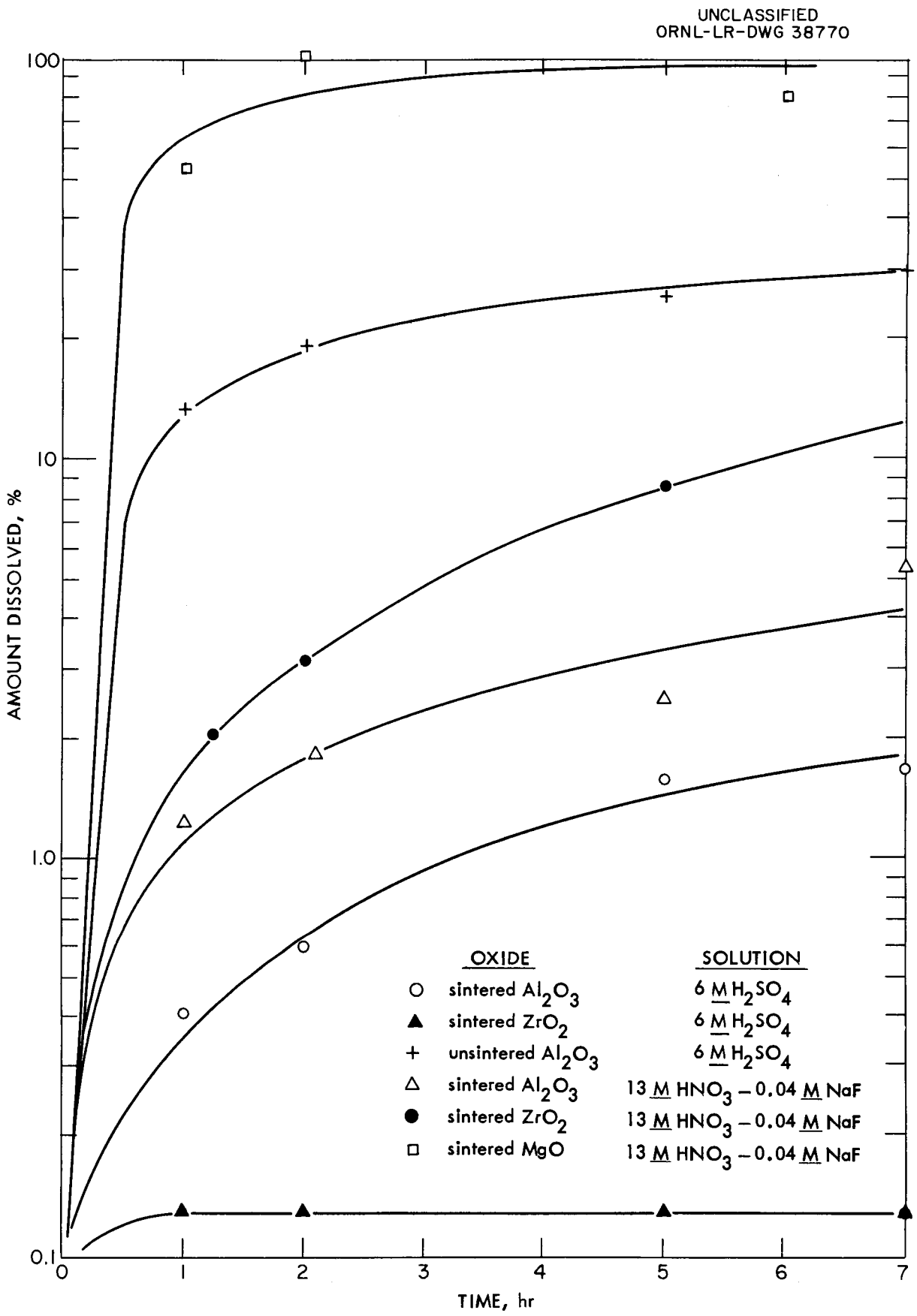

Fig. 6. Dissolution of refractory oxides in boiling 6 M H_2SO_4 and 13 M HNO_3-0.04 M NaF. Each oxide was sintered at 1400°C for 17 hr.

Table 5. Solubilities at 25°C of Some Neutron Poisons in Process Solutions

Compound	Solution	Solubility of B or Cd, M
H_3BO_3	4 M H_2SO_4	0.38, 0.41
	4 M H_2SO_4 + 5 g SS/l	0.36
	3.15 M H_2SO_4 + 42 g SS/l	0.56
	6 M H_2SO_4	0.30, 0.27
	6 M H_2SO_4 + 5 g SS/l	0.27
	5.4 M H_2SO_4 + 24 g SS/l	0.64
	13 M HNO_3	0.2 (ref. 16)
	13 M HNO_3	0.33 (ref. 17)
	13 M HNO_3-0.04 M NaF-0.04 M $Al(NO_3)_3$	0.25, 0.22
	8 M HNO_3-1 M $Th(NO_3)_4$-0.063 M $UO_2(NO_3)_2$	0.2-0.35 (ref. 18)
	8.65 M HNO_3-0.94 M $Th(NO_3)_4$-0.042 M $UO_2(NO_3)_2$	0.22
$Na_2B_4O_7$	2.95 M H_2SO_4	0.50
	3.70 M H_2SO_4 + 24 g SS/l	0.76
	1.80 M H_2SO_4 + 42 g SS/l	0.78
	5.0 M H_2SO_4	0.40
	8.65 M HNO_3-0.94 M $Th(NO_3)_4$-0.042 M $UO_2(NO_3)_2$	0.26
$CdSO_4$	3.73 M H_2SO_4	0.87
	3.00 M H_2SO_4 + 42 g SS/l	0.87
	5.55 M H_2SO_4	0.24
	4.88 M H_2SO_4 + 24 g SS/l	0.78
$Cd(NO_3)_2$	10 M HNO_3-0.04 M NaF-0.04 M $Al(NO_3)_3$	1.34
	8.65 M HNO_3-0.94 M $Th(NO_3)_4$-0.042 M $UO_2(NO_3)_2$	1.22

would be required prior to core dissolution, leading to a very high-volume process. Finding a suitable material of construction would be a serious problem.

In scouting experiments dissolution of sintered 96% ThO_2—4% UO_2 pellets was approximately 60% complete in 6 hr in boiling 2 M HCl—5 M HNO_3—0.04 M NaF. The presence of 0.04 M NaF in boiling 8 M H_2SO_4 resulted in about 1% dissolution of the pellets in 6 hr.

Table 6. Dissolution of Stainless Steels in Boiling Mixtures of Nitric and Hydrofluoric Acids

Type of Steel	Area of Sample, cm^2	Time, hr	Acid Solution HNO_3, M	Acid Solution HF, M	Vol. of Acid, ml	Average Rate mg/cm^2·min	Average Rate mils/hr	Final SS Conc., g/l
304L	31	6	1.0	1.0	150	0.28	0.82	21
	32		1.0	1.5	150	0.33	0.97	25
	31		1.0	2.0	150	0.42	1.2	31
	30		0.5	2.0	150	0.4	1.2	29
Carpenter 20	19.6	0.5	1.0	1.0	100	0.25	0.74	1.5
	20		13	0.04	100	0.2	0.59	0.78

3.6 Flowsheet Demonstration Experiments

Nine flowsheet demonstration experiments were performed with unirradiated simulated Consolidated Edison fuel pins, using 4 M H_2SO_4 as the decladding reagent. Each pin contained about 31 g of ThO_2-U_3O_8 pellets* and 31 g of stainless steel. Approximately 20% of the stainless steel was present as solid end caps. The pellets had been prepared by premixing the oxides with a binder before cold pressing. The binder was burned out at about 900°C, and the final pellets were obtained by sintering in air at 1600°C for about 14 hr. In the first seven experiments, Pyrex glassware was used in the decladding step and Teflon vessels in the core dissolution step. The tentative flowsheet (Fig. 1) was followed in most cases with solid-liquid separations being made by filtration. Runs 8 and 9 were performed in Carpenter 20 stainless steel apparatus. Runs 4-7 constituted a series of experiments in which four simulated fuel pins were dissolved in consecutive batch operations, with the solid residue from each dissolution being carried into the following cycle.

Uranium losses to the decladding solution were always less than 0.35% and were generally less than 0.05% (Table 7). The two cases where the uranium losses exceeded 0.1% (runs 8 and 9) were those in which the sulfuric acid excess was greater than 200%. Thorium losses were, in general, less than 0.1%. In runs 5-7, which were part of the four-cycle experiment, a heel of ThO_2-UO_2 was present during the decladding step. This had no apparent effect on the rate of dissolution of the cladding or on uranium or thorium losses. Uranium losses for the four cycles were 0.031, 0.026, 0.037, and 0.0041%, respectively, based on the total amount of uranium present in each cycle.

After the decladding step in runs 1-4, 8, and 9, approximately 92% of the ThO_2-UO_2 core was dissolved in 6 hr, starting with refluxing 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$ (Table 8). The use of a Carpenter 20 dissolver had no detectable effect on core dissolution. The percentage dissolution computed from the weight loss agrees very well with that obtained from thorium analyses whereas the uranium material balance was high in this series of experiments. In runs 5-7, the extent of dissolution in each

*The O/U ratio in these pellets was 2.75.

Table 7. Decladding of Simulated Consolidated Edison Reactor Fuel Pins With a 200% Stoichiometric Excess of Boiling 4 M H_2SO_4

Volume reduction during decladding = 6-10%

Run No.	Decladding Time, hr	Final H^+ Conc., M	Final SS Conc.,[a] g/liter	Loss to Decladding Solution, % U	Loss to Decladding Solution, % Th	SS Material Balance, %	SS Dissolved, %
1	5	2.07	-	<0.03	0.10	-	82
2	5	1.52	58	<0.001	0.03	99.9	78
3	6	3.17	62	0.04	0.05	93	85
4[b]	6	2.64	59	0.03	0.008	94	83
5[b]	6	3.02	69	0.03	0.003	93	-
6[b]	6	2.95	73	0.04	0.05	94	-
7[b]	6	2.96	59	0.004	0.05	95	-
8[c]	6	-	58	0.35	0.32	66	-
9[c]	6	2.54	65	0.25	0.06	100	73

[a]Based on the iron analyses of the undiluted decladding solution.

[b]Runs 4-7 were cyclic experiments in which the residue from each cycle was carried into the next.

[c]In runs 8 and 9 acid excesses were 250 and 600%, respectively.

Table 8. Dissolution of ThO_2-UO_2 Core Pellets after Decladding of Simulated Consolidated Edison Fuel with Boiling 4 M H_2SO_4

Core dissolvent: boiling 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$
Dissolution time: ~6 hr
Acid excess: 200%

Run No.	Final H^+ Conc., M	Fe in Core Solution, M	Core Dissolved, % By wt	Core Dissolved, % Analysis Th	Core Dissolved, % Analysis U	Material Balance,[a] % Th	Material Balance,[a] % U
1	8.9	-	92	92	107	99	115
2	-	-	95	101	128	106	133
3	9.3	0.0040	91	91	101	100	111
4	7.4	0.0054	90	92	121	102	132
5	7.0	0.0075	75	81	112	104	136
6	9.2	0.0076	84	82	111	95	124
7	7.3	0.018	86	75	102	87	114
8	7.6	0.0098	90	91	112	103	124
9	8.9	0.0064	93	92	112	97	118

[a]Based on an average of 31 g of pellets per pin having the composition 96% ThO_2—3.6 UO_2.

cycle became progressively lower (Fig. 7). This may be due to the fact that the acid excess used in each cycle was based only on the weight of pellets in a single fuel pin, the amount of ThO_2-UO_2 heel being neglected. Because of this, the actual acid excess decreased during the four cycles from 200% to 170%. As shown in Fig. 4a the rate of dissolution of ThO_2-UO_2 decreased with decreasing acid excess.

During the four-cycle experiment the iron concentration in the core solution, which increased steadily from 0.0054 M to 0.018 M, was directly related to the amount of stainless steel residue present in the system (Fig. 7). The stainless steel residue, which consisted mainly of solid end caps, continuously built up during the four cycles. On the other hand, the ThO_2-UO_2 heel reached a maximum after two cycles and diminished to an intermediate amount.

Another series of flowsheet demonstration experiments was performed, in which a 200% stoichiometric excess of boiling 6 M H_2SO_4 was used as the decladding reagent. As the decladding time increased from 3 to 5 hr, the amount of stainless steel dissolved increased from about 85% to about 97% (Table 9). Since approximately 20% of the stainless steel in each specimen was present as solid end caps, the data indicate that the 20-mil jacket is completely removed in 3 hr or less. The uranium loss to the decladding solution increased from about 0.04% in 3 hr to 0.1-0.2% in about 5 hr, while the thorium loss was always less than 0.04%. More experiments are required to confirm this trend. During the decladding operation, approximately 16% of the original volume was lost through hydrogen evolution and evaporation. After the decladding step, the core pellets were washed with a volume of cold water which was approximately equal to the volume of the decladding solution.

Table 9. Decladding of Simulated Consolidated Edison Reactor Fuel Pins with a 200% Stoichiometric Excess of Boiling 6 M H_2SO_4

Run No.	Decladding Time, hr	Volume Reduction, %	Uranium Loss, %	Thorium Loss, %	Stainless Steel Dissolved, %	
					By Analysis	By Wt
10	4.75	17	0.20	0.040	92.3	96.4
11	3	16	0.044	0.008	86.8	89.6
12	5	17	0.10	0.012	99.8	96.8

In the core dissolution step dissolution was essentially complete in about 18 hr in a 200% excess of dissolvent (Table 10), compared to the 92-95% expected in 6 hr. In run 10 a leak in the dissolver resulted in a volume reduction of 16% (the normal reduction is less than 5%), and, subsequently, a lower percentage of core dissolution. The sulfate concentration in the final core solution was about 0.1 M.

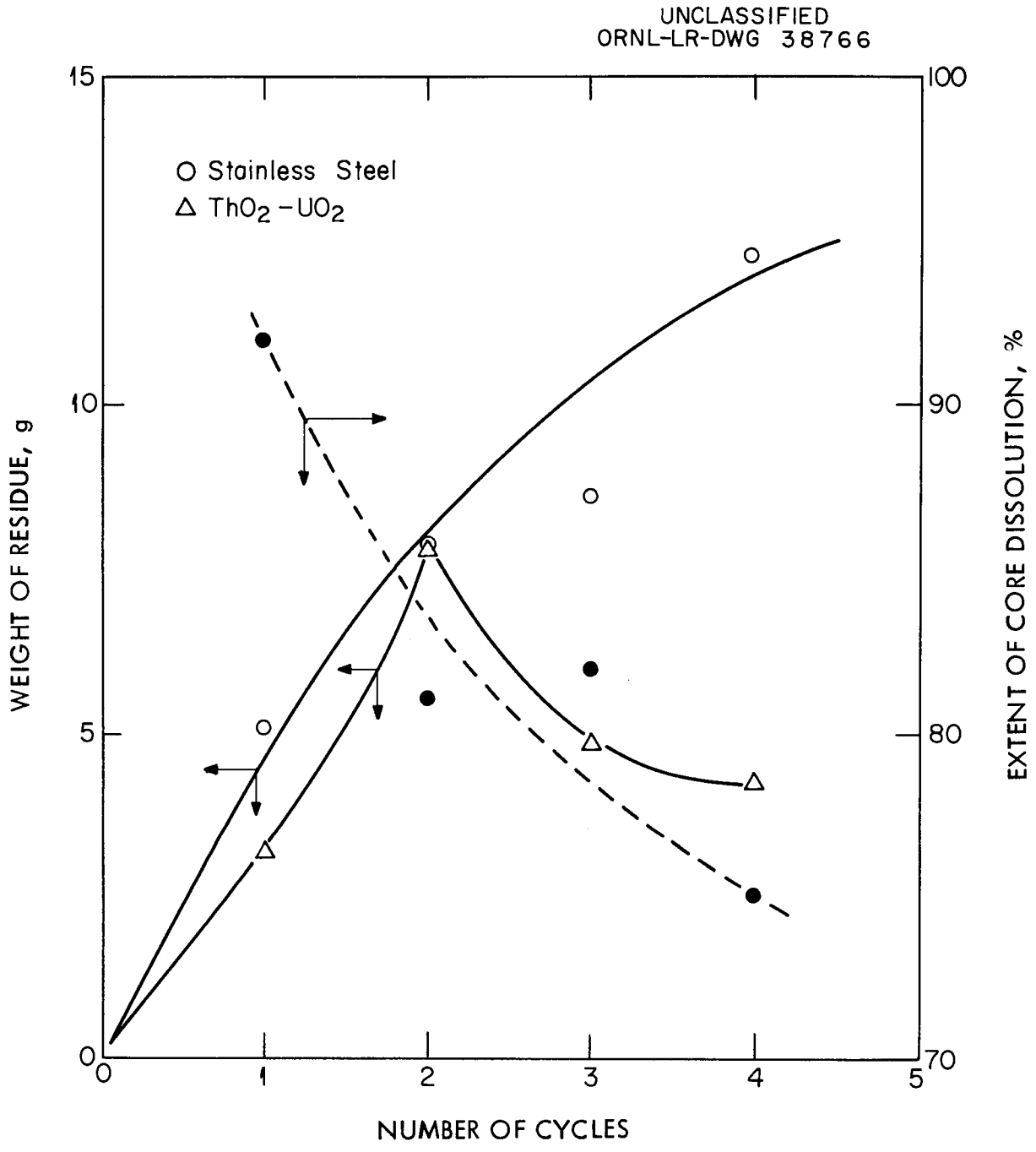

Fig. 7. Buildup of solids and decrease in percentage of core dissolution during successive cycles of the Consolidated Edison flowsheet with 4 M H_2SO_4.

Table 10. Dissolution of ThO_2-UO_2 Core Pellets after Decladding of Simulated Consolidated Edison Fuel Pins with 6 M H_2SO_4

Core dissolvent: boiling 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$
Acid excess: 200%

Run No.	Time, hr	% Dissolved by Th Analysis	% Dissolved by U Analysis	% Dissolved by Wt	$SO_4^=$ in Final Soln, M	Fe in Final Solution, M	Vol Reduction, %
10	6	83.8	85.4	-	0.14	0.017	16
11	18	99.8	99.9	100	0.06	0.0056	1.3
12	6	94.0	93.6	94.0	0.08	0.0038	0

4.0 FUTURE WORK

The following studies relative to the head-end dissolution of Consolidated Edison fuel appear essential before optimum flowsheet conditions can be chosen and final design of criticality safe pilot plant facilities can be made:

1. A study of the passivation of stainless steel in sulfuric acid and chemical methods for breaking the passivation.
2. Effects of cross-contamination of process solutions.
3. Solubilities of mixed neutron poisons in process solutions.
4. Uranium, thorium and plutonium losses during decladding of reactor grade specimens (O/U ratio = 2.06 or less).
5. Effect of irradiation on the rates of dissolution and losses.

Other areas include:

1. The effect of sintering temperature on the rate of dissolution of the ThO_2-UO_2 core pellets.
2. Addition of reagents to the sulfuric acid to suppress the dissolution of UO_2 and/or decrease the amount of hydrogen evolved.
3. Use of Darex[4] head-end process as an alternative decladding method.
4. Further studies of the effect of neutron poisons and corrosion inhibitors on the rates of decladding and core dissolution.
5. Factors that affect the rate of dissolution of UO_2 in sulfuric acid.

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