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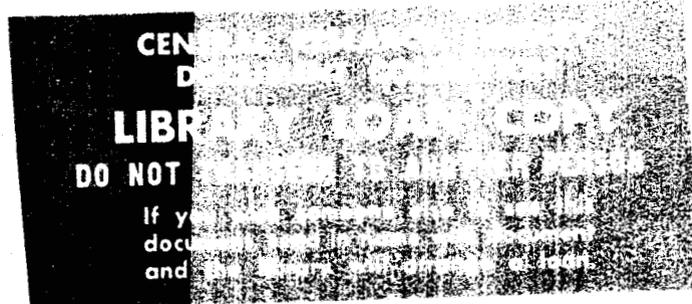
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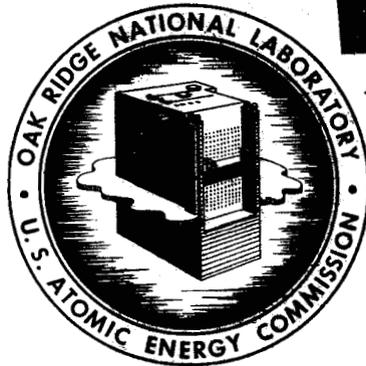
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UC-10 Chemistry-Separation Processes
for Plutonium and Uranium

DECLADDING OF CONSOLIDATED EDISON POWER
REACTOR FUEL BY SULFEX AND DAREX PROCESSES:
CYCLIC DISSOLUTION EXPERIMENTS

L. M. Ferris



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ORNL-2822

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

CHEMICAL DEVELOPMENT, SECTION B

DECLADDING OF CONSOLIDATED EDISON POWER REACTOR FUEL BY
SULFEX AND DAREX PROCESSES: CYCLIC DISSOLUTION EXPERIMENTS

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Based on data obtained in corrosion studies
at Battelle Memorial Institute by

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under Subcontract 988

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ABSTRACT

Simulated Consolidated Edison reactor fuel pins (95.5% $\text{ThO}_2\text{-U}_3\text{O}_8$ pellets encased in 304L stainless steel) were dissolved one-by-one according to the Sulfex and Darex flowsheets in Ni-o-nel and titanium vessels, respectively, 25 pins by each process. With boiling 5 M HNO_3 --2 M HCl (Darex), dissolution of the cladding was complete in each cycle with uranium losses of 0.1-0.4%. Dissolution of the $\text{ThO}_2\text{-U}_3\text{O}_8$ core pellets (which were about 80% of theoretical density) in boiling 13 M HNO_3 --0.04 M NaF --0.04 M $\text{Al}(\text{NO}_3)_3$ was also complete in each case. No problems arose from passivation of stainless steel or cross-contamination of solutions.

Two modifications of the Sulfex process were tested: (1) decladding with 200% excess of 6 M H_2SO_4 , and (2) initiating the reaction with 6 M H_2SO_4 and diluting to 4 M sulfate shortly thereafter. Uranium losses to the decladding solution were generally between 0.2 and 0.5% irrespective of the technique, but were as high as 0.9% in the presence of a $\text{ThO}_2\text{-U}_3\text{O}_8$ heel. The uranium losses were directly related to the amount of heel present. In most cases the fuel pins were passive to boiling 6 M H_2SO_4 and reaction was initiated by contacting the pin with a piece of iron. Core dissolution was less efficient than in the Darex tests, presumably because of sulfate contamination. Under the flowsheet conditions only 98-99% of the core was dissolved in each cycle.

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1.0 INTRODUCTION

This report gives data on buildup of end caps and uranium losses during decladding of stainless steel-clad $\text{ThO}_2\text{-U}_3\text{O}_8$ pellets, the rate of core dissolution, and the effect of cross-contamination of solutions in cyclic tests of the Darex¹ and Sulfex² processes. The decladding and dissolution experiments were conducted as part of a corrosion study at Battelle Memorial Institute, the results of which are being reported separately.³ Solutions obtained in the Battelle tests were forwarded to ORNL, where they were analyzed to obtain the data reported here.

At ORNL the solutions were sampled in preparation for analysis by J. F. Land. The analyses were made by the groups of G. R. Wilson and W. R. Laing of the ORNL Analytical Chemistry Division.

2.0 RESULTS

Simulated Consolidated Edison reactor fuel pins, consisting of 44.2 g of 95.5% $\text{ThO}_2\text{-U}_3\text{O}_8$ pellets (about 80% of theoretical density) encased in 25 g of 304L stainless steel, were dissolved according to the Darex (Fig. 1a) and Sulfex (Fig. 1b) flowsheets. The Darex dissolver was titanium and the Sulfex, Ni-0-nel. The decladding time was 3 hr in each process. In each pin was a wad of Kaowool to simulate the presence of a thermal insulation plug. Twenty-five pins were dissolved, one-by-one, by each method; however, only portions of the resulting solutions were analyzed. Solid residues were allowed to accumulate in successive cycles.

The Darex process appeared superior chemically to the Sulfex process in that no problems arose from passivation of stainless steel, cross-contamination, or instability of solutions. Uranium losses, for comparable decladding times, were essentially identical, but dissolution of the stainless steel was complete in a shorter time with the Darex process. Complete dissolution in boiling 5 M HNO_3 —2 M HCl of the stainless steel in pins of the type used in this study has been achieved in less than 1 hr;¹ however, in contrast, the stainless steel was not completely dissolved after 6 hr digestion with 6 M H_2SO_4 .²

The volume of waste decladding solution is nearly the same for each process. The decladding conditions chosen for the Darex tests were arbitrary, and the stainless steel concentration in the waste solution can probably be increased. The solubility of stainless steel sulfates in sulfuric acid limits the stainless steel concentration in the waste solution to essentially that obtained in these studies. In the event of high uranium losses to the decladding solution, recovery by solvent extraction is much easier with Darex than with Sulfex wastes because the Darex solution is easily processed in the standard tributyl phosphate-extraction system. Sulfate-bearing wastes must be greatly diluted with nitric acid before extraction with tributyl phosphate, or a second extractant such as an amine must be introduced into the extraction system.⁴

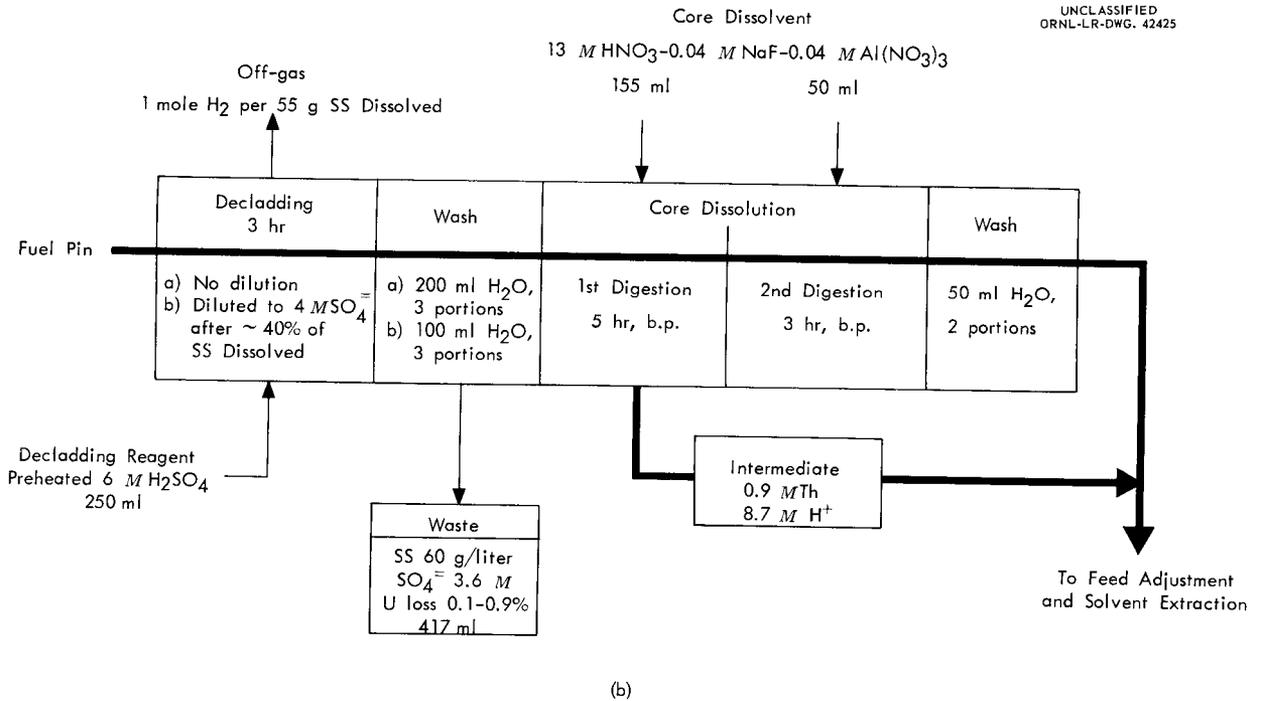
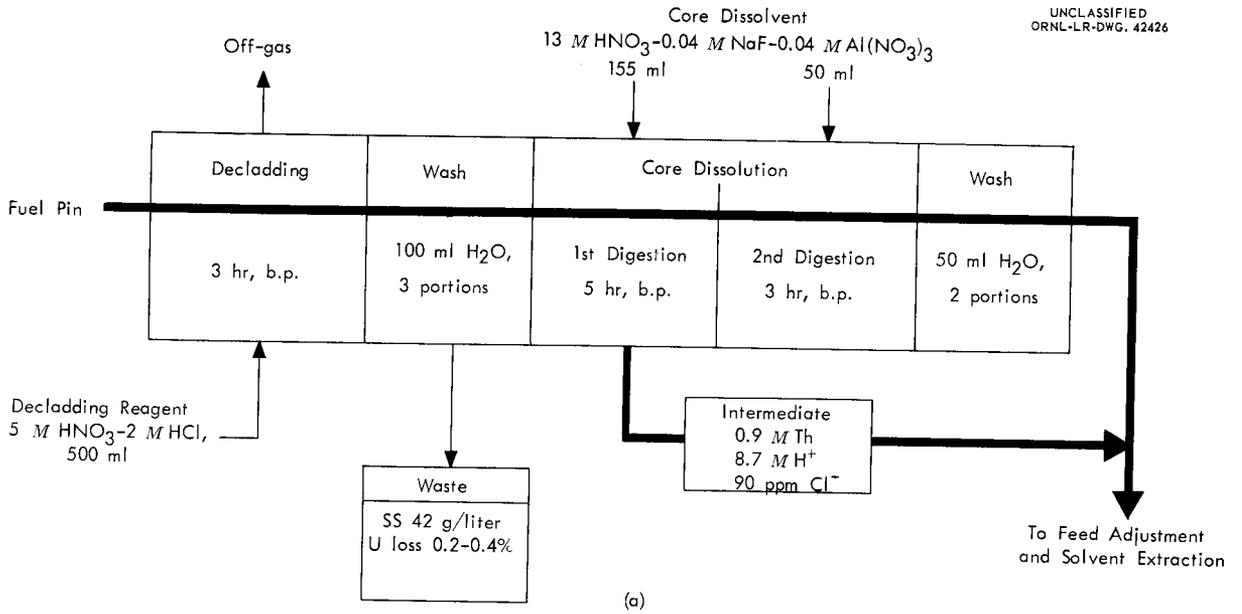


Fig. 1. Flowsheet for (a) Darex and (b) Sulfex decladding of Consolidated Edison fuel elements. Simulated fuel pin: 44 g of 95.5% ThO₂ - 4.5% U₃O₈ pellets clad with 25 g of type 304 stainless steel.

If the Sulfex process is to be used, adequate washing techniques must be devised. Not only must sulfate be kept out of the core dissolvent (Sect. 2.2), but also the presence of nitrate in the decladding solution must be avoided. The minimum-volume Sulfex process, decladding with 6 M H_2SO_4 and diluting the waste solution with the wash water, appears inoperable unless the spent decladding solution can be filtered hot. If it is allowed to cool, a precipitate of stainless steel sulfate is formed which must be removed by washing before core dissolution begins. Future studies should be concentrated on processes in which the decladding solution is diluted prior to filtration.

If a decladding procedure is used, complete dissolution of the core before the next decladding operation is mandatory to avoid higher uranium losses. Work now in progress⁵ shows that dissolution of high-density ($\sim 94\%$ of theoretical) pellets is difficult, and that the presence of iron aids in the dissolution. Only the Darex system lends itself to a total dissolution technique because cross-contamination by small amounts of solutions does not appreciably affect dissolution rates in the decladding and core dissolution cycles. Other inherent advantages of the Darex process are the facts that no hydrogen is evolved during decladding and that the decladding solution can be adjusted to recycle chloride and nitric acid--stainless steel nitrate solutions for use in subsequent cycles.⁶⁻⁸

2.1 Decladding

Darex Process. In each Darex cycle dissolution of the stainless steel cladding, including end caps, was essentially complete in 3 hr. The only exceptions were runs in which 400 ml instead of 500 ml of decladding solution was used. After dilution with the wash water according to flowsheet conditions, the waste solution contained an average of 45 g of stainless steel per liter. In no case was a stainless steel specimen passive to boiling 5 M HNO_3 --2 M HCl. The use of Darex decladding would therefore minimize any problems associated with passivation of stainless steel and end-cap buildup.

In the 25 Darex cycles, the uranium loss to the decladding solution varied randomly between 0.1 and 0.4% (Table 1). These losses are identical with those obtained in studies at ORNL.⁹ All Darex cycles were identical except for the first three runs where 400 ml of boiling 5 M HNO_3 --2 M HCl was used for decladding instead of the 500 ml used in the other 22 runs.

Sulfex Process. The amount of end caps increased slowly with increasing number of cycles. Under the best operating conditions, runs 11-25 where the acid was diluted to 4 M sulfate shortly after the reaction was started, the end cap residue increased gradually from about 3 to 7 g (Fig. 2). This corresponds to about 80% dissolution of the stainless steel present at the start of each cycle. When actual fuel assemblies are reprocessed, the buildup of end caps may not be serious because of the lower ratio of weight of end caps to weight of tubing in the 99-in.-long Consolidated Edison fuel pins.¹⁰ With either Sulfex procedure given in Fig. 2 the waste

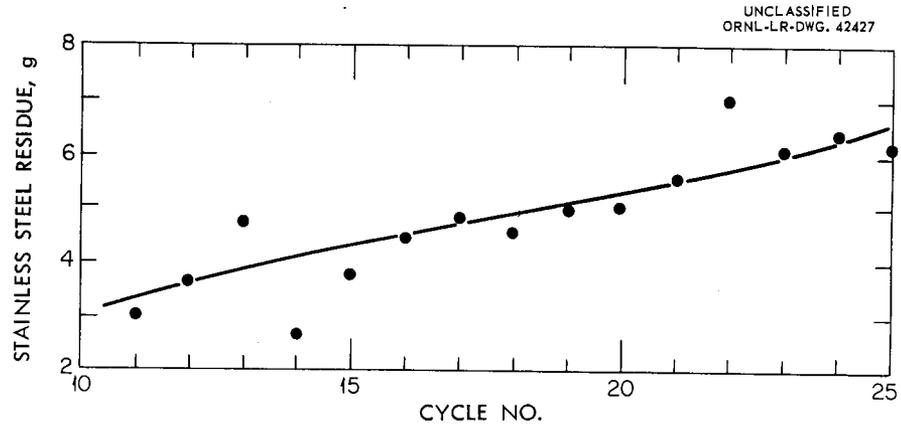


Fig. 2. Weight of end caps as a function of Sulfex dissolution cycles. New pin containing 25 g of stainless steel added in each cycle. Dissolution started with 200% excess of 6 M H_2SO_4 ; solution diluted to 4 M sulfate after about 40% of the stainless steel had dissolved.

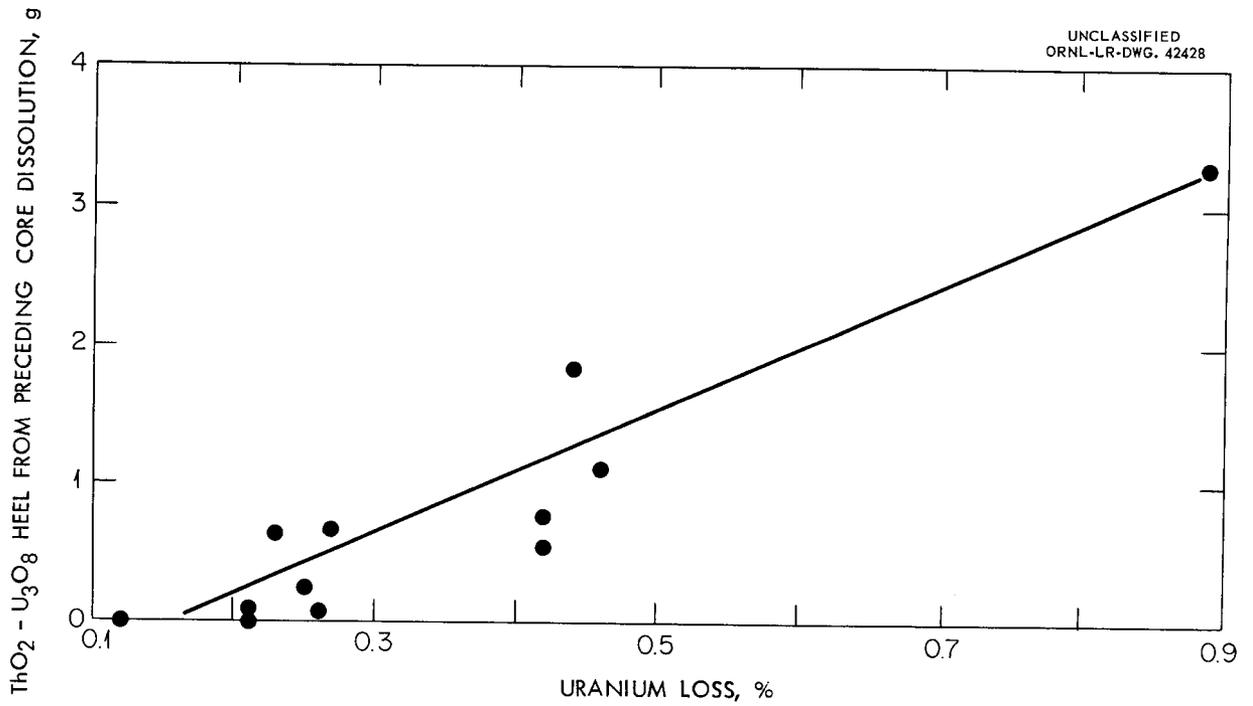


Fig. 3. Uranium loss to sulfuric acid decladding solutions as a function of weight of $ThO_2-U_3O_8$ remaining from preceding core dissolution.

solution contained about 60 g of stainless steel per liter.

Table 1. Stainless Steel Dissolution and Uranium Losses in 11 of the 25 Cyclic Tests of Darex Flowsheet for Consolidated Edison Power Reactor Fuel

Decladding solution: 5 M HNO₃ - 2 M HCl

Decladding time: 3 hr

Run No.	Stainless Steel Dissolved, %		Stainless Steel Conc. in Waste, g/liter	Uranium Loss, %
	By Weight	By Analysis		
Ti-1 ^a	69.2	51.4	36.7	0.16
4	96.8	116	52.4	0.20
6	98.6	105	46.1	0.24
8	100	99.0	43.4	0.17
11	100	102	44.4	0.24
14	100	105	46.1	0.27
18	100	104	45.3	0.41
19	100	99.9	43.1	0.31
21	100	99.4	43.0	0.41
23	100	99.8	43.0	0.28
25	100	99.4	43.0	0.31

^aonly 400 ml of decladding reagent used.

In nearly all cases the stainless steel was passive to boiling 6 M H₂SO₄ although the nitrate concentration in the undiluted waste solution was less than 0.009 M (Table 2). An initial nitrate concentration of greater than 0.01 M is required to cause passivation of nonoxidized, unirradiated stainless steel.^{2,11} The passivation problem was alleviated somewhat by heating the acid to boiling in a glass vessel before adding it to the Ni-o-nel dissolver. Heating of the acid in the dissolver in the presence of stainless steel end caps and residue may have resulted in dissolution of sufficient stainless steel to cause passivation of a fresh fuel pin.² In all but two cases passivation was easily broken by touching the fuel pin with a nail or scratching it with a file. The two pins that could not be depassivated in this way were dissolved in Darex tests with no difficulty.

Uranium losses in the Sulfex experiments varied randomly from 0.1 to 0.9% (Table 2). In studies at ORNL,² where only one pin was dissolved before the dissolver was cleaned out, losses were 0.1-0.2%. In the cyclic tests, however, a heel of ThO₂-U₃O₈ core pellets was always present during decladding owing to the inefficiency of core dissolution (Sect. 2.2). The uranium losses were directly related to the amount of ThO₂-U₃O₈ present during decladding (Fig. 3).

Table 2. Decladding of Simulated Consolidated Edison Fuel Pins by the Sulfex Process

Decladding time: 3 hr

Run No.	Stainless Steel Dissolved, ^a %		Stainless Steel Concentration in Waste, g/liter	NO ₃ ⁻ Concentration in Undiluted Decladding Solution, M	Uranium Loss, %
	By Weight	By Analysis			
Decladding solution: 6 M H ₂ SO ₄ , 200% excess					
N-1	84.4	76.4	46.0	0.006	0.12
3	81.3	79.1	59.7	0.005	0.25
6	81.1	76.2	57.6	0.0077	0.44
9	70.7	69.2	49.8	0.0087	0.89
Decladding solution: 6 M H ₂ SO ₄ 200% excess, diluted to 4 M SO ₄ ⁼					
11	87.9	84.4	42.6	0.020	0.76
12	86.8	84.2	52.6	0.0040	0.21
14	91.0	88.3	65.3	0.0050	0.21
16	84.4	81.0	65.6	0.0049	0.23
18	84.6	83.7	64.0	0.0047	0.42
19	83.1	77.6	58.6	0.0056	0.42
21	81.5	71.9	71.0	0.0038	0.27
23	81.1	81.1	69.6	0.0050	0.46
25	80.5	76.5	72.6	0.0046	0.26

^a based on total amount of stainless steel present at beginning of each cycle.

In the first 10 Sulfex runs, decladding was achieved with a 200% excess of boiling 6 M H₂SO₄ and the resulting solution diluted with only the 0.8 volume of water used to wash out the dissolver. In runs 11-25 the decladding solution was diluted to 4 M sulfate after about 40% of the cladding had dissolved, and the dissolver was then washed with 0.4 volume of cold water. After core dissolution, the wash water was boiled to help remove nitrate.

2.2 Core Dissolution

Darex Process. In the Darex tests, dissolution of the core was complete in each cycle under flowsheet conditions. As predicted from previous rate studies,^{2,12} 91-95% of the core was dissolved in the first, 5-hr, digestion with a 200% excess of boiling 13 M HNO₃-0.04 M NaF-0.04 M Al(NO₃)₃ (Table 3). The chloride concentration in the product of the first dissolution varied randomly from 40 to 90 ppm.

Table 3. Dissolution of 95.5% ThO₂-4.5% U₃O₈ Core Pellets after Darex Decladding of Simulated Consolidated Edison Fuel Pins in Cyclic Tests

Pellets: ~80% of theoretical density

1st 5-hr core digestion: 200% excess of boiling 13 M HNO₃—
0.04 M NaF—0.04 M Al(NO₃)₃

Run No.	Pellets Dissolved, %		Cl ⁻ Conc. in Product of 1st Digestion, ppm	H ⁺ Conc. in Product of 1st Digestion, M
	1st Digestion	Total under Flowsheet Conditions		
Ti-1	93.3	100	42	8.70
4	91.8	100	68	8.68
6	95.8	100	48	8.55
8	93.8	100	64	8.48
11	91.0	100	40	8.73
14	94.0	100	66	8.61
18	93.4	100	48	8.68
19	95.9	100	65	8.61
21	95.2	100	75	8.51
23	95.2	100	70	8.59
25	95.9	100	85	8.61

Sulfex Process. Core dissolution after decladding with sulfuric acid proved much more difficult. Only about 80% of the core dissolved in the first, 5-hr, digestion with 200% excess of boiling 13 M HNO₃—0.04 M NaF—0.04 M Al(NO₃)₃ (Table 4). In only one case was dissolution complete after two digestions. The diminution in dissolution rate was probably caused by contamination of the core dissolvent with sulfate. As the sulfate concentration in the core dissolvent increases, the rate of core dissolution decreases.¹³ As little as 0.05 to 0.1 M sulfate in the core dissolvent markedly decreases the reaction rate. It is postulated that sulfate ion reacts at the surface of the pellets to produce a very insoluble¹⁴ film of thorium sulfate, through which diffusion of reactant and/or product ions is probably slow.

The presence of sulfate in the core dissolvent in the first 10 runs is easily explained. Even though the decladding solutions were filtered while still hot, a precipitate of stainless steel sulfates formed and was not completely removed by the subsequent water wash. In runs 11-25 diluting from 6 to 4 M sulfate should have produced a solution which could be cooled to room temperature without precipitation,² and was generally the case. However, sufficient sulfate may have been sorbed by the Kaowool and pellets to cause the observed decrease in reaction rate.

In nearly all cases the solution obtained after the first core digestion contained a precipitate with a sulfate content of about 40%. No correlation of the extent of core dissolution and the weight of precipitate was obtained.

Table 4. Dissolution of 95.5% ThO₂-4.5% U₃O₈ Core Pellets after Sulfex Decladding of Simulated Consolidated Edison Fuel Pins in Cyclic Tests

Pellets: 80% of theoretical density
 1st 5-hr core digestion: 200% excess of boiling 13 M HNO₃-
 0.04 M NaF-0.04 M Al(NO₃)₃

Run No.	Pellets Dissolved, %		SO ₄ ⁼ Conc. in Product of 1st Digestion, M
	1st Digestion	Total under Flowsheet Conditions	
N-1	1.5	1.5	0.61
3	68.8	94.7	0.04
6	77.0	98.3	0.053
9	67.2	90.5	0.04
11	86.0	100	0.04
12	77.4	99.8	0.10
14	80.2	99.6	0.10
16	87.0	97.7	0.10
18	80.1	98.2	0.10
19	66.2	96.9	0.10
21	75.0	99.1	0.10
23	80.4	98.9	0.10
25	80.2	99.9	0.10

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