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DISSOLUTION OF IRRADIATED CONSOLIDATED
EDISON POWER-REACTOR FUEL BY THE
SULFEX AND DAREX PROCESSES

by

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Losses of fertile and fissile materials during chemical decladding of irradiated prototype Consolidated Edison power-reactor fuel pins by the Sulfex and Darex processes were determined, on a laboratory scale, in all-glass apparatus. For air-fired low-density (~85 per cent of theoretical) fuel cores, minimum losses of uranium, thorium, and plutonium were in the 0.1 to 0.2 per cent range, by either process. These losses increased if the dejacketed cores were allowed to remain in contact with the cladding solution. No selectivity of dissolution of core components was apparent. Comparable losses were obtained with similar unirradiated fuel pins.

Irradiated core pellets showed a tendency to shatter. When shattered core pellets were present, losses to the cladding solution were excessive. Losses of from 0.5 to 4.5 per cent were observed, depending on the extent of core fragmentation and the time of contact with the cladding solution. No correlation between burnup and extent of shattering was discernible.

Core dissolution times were not lengthened by irradiation to the 175 to 300-MWD/T core level.

INTRODUCTION

The Chemical Technology Division of the Oak Ridge National Laboratory has for several years been engaged in the development of chemical methods for processing the advanced fuel types proposed for use in power reactors. The basic unit process for the recovery and decontamination of fertile and fissile materials is aqueous solvent extraction. Prior to solvent-extraction reprocessing, it is necessary to convert the fuel materials to an aqueous solution. The results and current status of this work are summarized in the literature. (1-3)

One of the fuels for which the Oak Ridge National Laboratory has been assigned reprocessing responsibility is the Consolidated Edison power-reactor fuel. This is a highly enriched $\text{UO}_2\text{-ThO}_2$ fuel, stainless steel clad. Two aqueous head-end processes, Sulfex and Darex, are being developed to convert this fuel to a solution suitable for solvent-extraction processing. Many data are already available on unirradiated fuel. Only limited data are available on the effects of fuel irradiation on the amenability of fuel elements to these processes. The data presented in this report were obtained as a supplement to this phase of the development program.

(1) References are at end of text.

EXPERIMENTAL PROCEDURE

All experiments were performed in the apparatus shown schematically in Figure 1. A photograph of the apparatus as used in the hot cell is shown in Figure 2. Of all-glass construction, it consisted of a dissolver, filter, intermediate filtrate receiver, and product receiver, plus the necessary auxiliary lines and equipment. To minimize the vertical height of the apparatus, as well as to minimize the foaming problem, a horizontal dissolver was used. This also eliminated the need for a basket to charge the fuel pin; the fuel pin was readily slid in through the inclined charging port at one end. Early Sulfex runs were made in a 2-1/4-in. -diameter by 10-in. -long dissolver. Darex dissolutions required a larger vessel (3 in. in diameter by 12 in. long), which was also used for later Sulfex dissolutions.

Both cladding and core solutions were filtered through a 60-ml fritted-glass filter (medium frit). All transfers and all filtrations were by vacuum. The filter was set up to permit reversing the vacuum on it and this was occasionally helpful in improving the filtration rate. Capillary tubing was originally installed for all liquid-transfer lines to minimize liquid holdup. Although this performed satisfactorily with unirradiated pins, in which there was no shattering, it had to be replaced by 7-mm tubing to eliminate plugging by core fragments for the experiments with irradiated pins.

In the Sulfex experiments, the fuel pins were introduced into 250 ml of boiling 6 M H_2SO_4 to minimize occurrence of passivation of the stainless steel cladding. Samples of cladding solution were withdrawn after refluxing for 3 hr at 110 to 115 C, by which time decladding was complete, except for the end plugs. The dejacketed core pellets were refluxed with the decladding solution for another 3 to 5 hr, after which the entire decladding solution was withdrawn, filtered, collected, and measured. The interim samples were originally taken by filtering a portion of the decladding solution, any excess being returned to the dissolver through the transfer lines. Later, cladding-solution samples were pipetted directly from the dissolver, to minimize the danger of contamination by any residual core solution lodged in the system.

The dissolver and filter were washed with three 33-ml portions of water, the washings were combined with the main decladding solution, and the composite solution was sampled for analysis. The apparatus and dejacketed core pellets were then thoroughly washed, to minimize carry-over of sulfate ion to the core-dissolution step. These washings were discarded.

Core dissolution was achieved in two steps. In the first, core dissolvent [155 ml of 13 M HNO_3 -0.04 M NaF-0.10 M $\text{Al}(\text{NO}_3)_3$] was added either directly to the dissolver, or, if necessary, first passed through the filter to dissolve solids from the decladding step for return to the core dissolution. In one test, in which carry-over of fragments to the filter with the decladding solution was noticeable, the core-dissolvent solution was also occasionally circulated through the filter during core dissolution. After 5 hr of refluxing, which normally dissolved 90 to 95 per cent of the core, the first core solution was withdrawn, filtered, its volume measured, and sampled. The remaining core residue was dissolved by refluxing for 3 hr with 50 ml of fresh core dissolvent. After filtering, measuring, and sampling this second core solution, the dissolver was

FIGURE 1. SCHEMATIC OF FUEL-PIN-DISSOLUTION APPARATUS

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FIGURE 2. FUEL-PIN-DISSOLUTION APPARATUS AS SET UP IN THE HOT CELL

washed with two 25-ml portions of water. A composite core solution was prepared, based on the volumes of the three solutions collected.

The apparatus was again thoroughly washed to minimize nitrate carry-over to the next cladding dissolution. Any end-plug residues remaining were also removed at this time.

Procedure for decladding by the Darex process was similar, the principal deviations from the Sulfex procedure being the use of cold initial acid (500 ml of 5 M HNO_3 -2 M HCl) and a shorter dissolution time (1 hr). Core-dissolution procedures were identical.

UNIRRADIATED CONSOLIDATED EDISON FUEL PINS

Preliminary dissolutions were conducted on six unirradiated prototype Consolidated Edison fuel pins supplied by the Chemical Technology Division of ORNL, using the dissolution apparatus and procedures later used for the irradiated specimens. These pins were approximately 3/8 in. in diameter by approximately 7 in. long, and contained about 25 g of stainless steel and 44 g of core pellets. Markings on the package indicated that the pins had been subjected to heat-cycling tests, as did their appearance. All were noticeably warped and possessed oxidized surfaces.

Sulfex Process

Three unirradiated pins were dissolved by the Sulfex process, using the process conditions established by the Chemical Technology Division.⁽⁴⁾ In this process, the stainless steel jacket is selectively dissolved by refluxing in 200 per cent stoichiometric excess of 6 M H_2SO_4 . No temperature data are available on the dissolutions of the irradiated specimens; preliminary experiments with stainless steel indicated reflux temperatures were in the 110 to 115 C range. After removal of the cladding solution and washing with water to remove residual sulfate, the core pellets were dissolved in a two-pass process using 13 M HNO_3 -0.04 M NaF -0.04 M $\text{Al}(\text{NO}_3)_3$. On the basis of corrosion data $\text{Al}(\text{NO}_3)_3$ concentration was later increased to 0.1 M, at the suggestion of the Chemical Technology Division.

Passivation of the stainless steel was observed only in the first run, C-1. Two 4-ml additions of formic acid, each calculated to make the sulfuric acid about 0.1 M in formic acid, were ineffective, possibly because the formic acid appeared to flash off almost immediately upon addition to the boiling sulfuric acid. Touching the pin with a steel rod broke the passivation, after which dissolution of the cladding proceeded smoothly.

Rate of hydrogen evolution was measured in the manually operated Sulfex dissolutions by means of a rotameter in the off-gas line. The use of a rotameter did not prove practical in the remotely operated runs. Based on indicated gas flows, rate of attack of the oxidized cladding on these fuel pins was lower than for sheet stainless steel

of corresponding surface area and weight. Hydrogen evolution never completely ceased, dropping to a steady minimum when only the end plugs remained.

Run C-2 was also performed manually in the laboratory. Other than a slightly shorter decladding time, it differed only from Run C-1 by the absence of passivation.

Run C-5 was conducted at the BMI Hot Cell Facility, primarily to check performance of the dissolution apparatus when remotely operated. Passivation was absent. The effect of prolonged contact of the declad core pellets with refluxing cladding solution (air blanketed) on uranium losses was checked in this experiment. Small filtered samples of cladding solution were withdrawn after 3 and 4 hr; the balance of the cladding solution was withdrawn after 6 hr. Uranium loss to the cladding solution at 3 hr was 0.22 per cent; this increased to 0.23 and 0.39 per cent in the subsequent periods.

Washing of the apparatus after the cladding dissolution was evidently insufficient in this run, as there was a substantial carry-over of sulfate to the core dissolution. Heavy crystallization of thorium sulfate in the core solutions resulted, and dissolution of the core was incomplete (3.0 g of residue). Analysis of the composite core solution indicated it was about 0.15 M in sulfate. Sulfate concentration during the first step is calculated to have been nearly 0.25 M.

Analytical data for the Sulfex and Darex runs on unirradiated fuel pins are shown in Tables 1 and 2.

Although the insoluble residues (combined cladding and core) retained by the glass-frit filter were weighed for each experiment, uranium analyses were obtained only on those from Runs C-1 and C-2. Uranium contents were only 0.04 to 0.07 per cent. Since the typical acid-insoluble residue (which appeared to consist essentially only of Kaowool from the end plugs and silica from the stainless steel) weighed but 0.26 to 0.33 g, uranium losses to these residues were insignificant.

Losses of uranium to Sulfex decladding solutions were in the 0.3 to 0.4 per cent range. On a percentage basis, thorium losses were lower by almost an order of magnitude (0.03 to 0.05 per cent), indicating some selectivity in leachability. Such behavior is not unreasonable considering the nature of the unirradiated core pellets. These maintained their integrity throughout the decladding step, unlike some of the irradiated core specimens, and presented a minimum surface to attack. However, based on data from the Chemical Technology Division, the uranium oxide in these air-fired cores had a high oxygen-to-uranium ratio, approaching that for U_3O_8 , and would be expected to be more readily soluble than the specified UO_2 . The higher-than-expected losses, for both uranium and thorium, can also be attributed partly to the low densities of the core pellets (80 to 85 per cent of theoretical, on the basis of data from ORNL). Lowering of the density has been shown⁽³⁾ to substantially increase uranium losses.

TABLE 1. ANALYSES OF CLADDING SOLUTIONS FROM DISSOLUTIONS OF UNIRRADIATED CONSOLIDATED EDISON FUEL PINS

Run	Dissolution Time, hr	Cladding Solution				Iron Concentration, g per liter	Original Weight of Pin, g	End-Plug Residue, g	Filtered Residue ^(b)	
		Uranium		Thorium					Weight, g	Uranium, per cent
		Concentration, g per liter	Loss ^(a) , per cent	Concentration, g per liter	Loss ^(a) , per cent					
Sulfex C-1	4	0.0195	0.35	0.035	0.028	46.0	69.3	2.52	0.33	0.076
Sulfex C-2	3	0.0166	0.31	0.055	0.046	52.0	69.3	2.26	0.26	0.042
Sulfex C-5	6	0.0269	0.39	0.062	0.043	46.0	69.4	2.32	3.0	--
Darex C-3 ^(c)	2	0.0230	0.63	0.074	0.092	31.5	69.3	3.34	0.09	0.060
Darex C-4	1	0.0067	0.23	0.065	0.102	21.2	69.4	0.15	0.12	0.015

(a) Based on an input of 1.7 g of uranium and 36.9 g of thorium.

(b) Acid-insoluble residue recovered from filter after filtration of both cladding and core solutions.

(c) Two-pass dissolution with 400 ml of Darex solution.

TABLE 2. ANALYSES OF CORE SOLUTIONS FROM DISSOLUTIONS OF UNIRRADIATED CONSOLIDATED EDISON FUEL PINS

Run	Solution	Volume, ml	Uranium		Thorium		Iron Concentration, g per liter	Sulfate Concentration, g per liter	Free Acidity, N
			Concentration, g per liter	Weight, g	Concentration, g per liter	Weight, g			
Sulfex C-1	First core	166	--	--	196	32.6	--	--	--
	Second core	42	--	--	83	3.5	--	--	--
	Composite(a)	305	5.31	1.62	122	37.2	0.32	1.6	7.8
Sulfex C-2	First core	160	--	--	195	31.2	--	--	--
	Second core	92	--	--	64.5	6.1	--	--	--
	Composite(a)	254	6.68	1.70	152	38.6	0.33	2.0	7.9
Sulfex C-5	First core	~125	--	--	169	21.1	--	--	--
	Second core	100	--	--	104	10.4	--	--	--
	Composite(a)	225	7.50	1.68	146	32.7	2.7	14.5	8.0
Darex C-3	First core	160	--	--	231	36.9	--	--	--
	Second core	50	--	--	31.5	1.6	--	--	--
	Composite(a)	255	6.78	1.77	154	39.2	0.49	--	7.8
Darex C-4	First core	165	--	--	204	34.7	--	--	--
	Second core	50	--	--	105	5.2	--	--	--
	Composite(a)	260	7.58	1.97	154	40.1	0.26	--	7.8

(a) Composite prepared by taking 1/5 aliquots of core and wash solutions.

Darex Process

Three unirradiated Consolidated Edison fuel pins were dissolved by the Darex (dilute aqua regia) process. In this process, the stainless steel jacket is selectively dissolved by refluxing in approximately 200 per cent excess acid, in this case 5 M HNO_3 -2 M HCl . Introduction of the pin into boiling acid is not necessary, since passivation is not normally a problem with this system and the dissolution is begun with the acid at ambient temperature or a little above. Decladding is more rapid than with Sulfex and is complete, including end plugs, in 1 hr. Use of an HNO_3 - HCl cladding dissolvent eliminates the danger of sulfate contamination in the core-dissolution step, which is identical for both processes.

Two manually operated Darex dissolutions were conducted in the laboratory. The small dissolver fabricated for the Sulfex experiments was used for the first run (Run C-3), which necessitated reducing the quantity of cladding dissolvent below that called for by the flow sheet. The cladding was dissolved in two passes. In the first pass, 1 hr at the boiling point with 250 ml of dissolvent dissolved all of the jacket except the end caps and a little granular stainless steel residue. The second pass consisted of 1 hr at the boiling point with 150 ml of fresh dissolvent. The decladding solutions were combined for analysis. Uranium loss was higher in this experiment than in the succeeding Darex run, probably as a result of the additional 1-hr contact of the dejacketed pellets with fresh dissolvent.

One of the major disadvantages of the proposed Darex decladding process is the larger volume of highly radioactive cladding solution than results from Sulfex decladding. The data from this test suggest that it might be possible to dejacket with only about a 100 per cent stoichiometric excess of Darex dissolvent, which would approximately equalize the volumes of cladding waste solutions. If smaller volumes of wash and dilution water could be used, which seems possible, Darex waste solutions might even be smaller than Sulfex waste solutions.

A new and larger dissolver (3 in. in diameter by 12 in. long, sized to hold 500 ml of dissolvent) was used for the second manually operated Darex dissolution (Run C-4). The entire jacket, including end plugs, was dissolved after 1 hr digestion at the boiling point. A very slight sandy residue remained in the dissolver, along with the core pellets. This was retrieved at the conclusion of the core dissolution. Its total weight was only 0.15 g (including 0.03 g of Kaowool) and uranium content was negligible (0.007 per cent).

Acid-insoluble residues from the cladding and core dissolutions retained by the filter in these two experiments were smaller and contained less uranium than the corresponding residues from the Sulfex runs. Weights were 0.09 to 0.12 g and uranium contents only 0.02 to 0.06 per cent.

Analytical data for these runs are compared with those of the Sulfex dissolutions in Table 1. Uranium losses, immediately upon decladding, appeared to be comparable for both Sulfex and Darex. Thorium losses appeared to be somewhat greater for Darex on the basis of the few experiments made.

A third run was conducted at the Hot-Cell Facility to check the performance of the apparatus when remotely operated. Analyses were not obtained for this run.

IRRADIATED CONSOLIDATED EDISON FUEL PINS

Dissolutions of irradiated fuel pins were performed remotely in a hot cell using the same laboratory-scale all-glass apparatus used for the dissolutions of unirradiated pins.

Six ORR-irradiated prototype Consolidated Edison fuel pins, furnished by ORNL were used for the experimental dissolutions. These 3/8-in. -diameter by approximately 7-in. -long pins reportedly consisted of a 20-mil jacket of Type 304L stainless steel, capped at each end by a 1/2-in. end plug. Total weight of stainless steel was about 27 g. The core consisted of 42 to 43 g of 0.27-in. -diameter by 3/8-in. pellets with a nominal composition of 95 w/o ThO₂-5 w/o UO₂ (natural uranium). Gross pin weights ranged from 69.31 to 70.73 g.

Based on data from the Chemical Technology Division⁽⁵⁾ these pins, plus 12 analogous pins used in similar dissolution studies at ORNL, were irradiated as a group in the ORR for one cycle at a nominal flux of 10^{14} n/(cm²)(sec). Three bundles of six pins each were in the irradiation capsule which was therefore fairly long. This probably accounts for the variations in exposure. Burnup data indicate the six pins ranged from 175 to 300 MWD/T core. A stereomicroscope was available in the hot cell, and, with its aid, it was possible to decipher the identification numbers on each pin. If the pin locations during irradiation are known, these data may assist in correlating burnup results for the other 12 pins.

Data available on the fabrication of these pins⁽⁵⁾ indicate that they were quite comparable to the unirradiated prototypes. The core pellets were of low density and had been air fired rather than hydrogen fired so that oxygen-to-uranium ratios were high, about UO₂.7.

Sulfex Process

Four irradiated prototype Consolidated Edison fuel pins were dissolved by the Sulfex process under the same conditions used for the unirradiated specimens except that the Al(NO₃)₃ concentration in the core dissolvent was increased to 0.1 M after the first run at the suggestion of the Chemical Technology Division. The cladding solution was not withdrawn after the standard 3-hr decladding period. Instead, after sampling, the dejacketed core pellets were refluxed with the cladding solution for an additional 3 to 5 hr to determine the effects of contact time on core losses.

In the first experiment (Run S-1), a 70.73-g pin (A-103) was introduced into 250 ml of 6 M H₂SO₄ in the horizontal dissolver. Prior examination of this pin under a stereomicroscope had shown the surface to be clean and bright, free from significant oxidation. There was no passivation, and attack was immediate and vigorous. After 3 hr a small portion of the cladding solution was filtered through the glass-frit filter. Approximately 20 ml of this solution was transferred to the product receiver and withdrawn for samples with the balance being returned to the dissolver. The cladding solution was sampled similarly at 6 hr. After 8 hr the cladding solution was filtered off, and the dissolver and core pellets were washed with three 33-ml portions of water. The cladding solution was combined with the washings and sampled.

After thoroughly washing the dissolver, several core pellets ranging in length from 1/4 to nearly 1/2 in. were withdrawn for examination. The density of one of the larger pieces was determined by displacement to be 8.52 g per cm³, approximately 87.5 per cent of theoretical.

To effect dissolution, 155 ml of cold 13 M HNO₃ core dissolvent was added to the dissolver and heated to the boiling point. The dissolver vessel failed after about 1/2 hr, presumably the result of thermal shock. Approximately 18.9 g of undissolved material was recovered, of which about 6.4 g was end-cap material. Although most of the loss appeared to be due to dissolution, there was also considerable fragmentation of some of the core pellets into pieces too small to recover. The recovered core material was dissolved in a new dissolver, using 100 ml of core dissolvent. Some core material remained after 5 hr, and this was dissolved by a second pass with 50 ml of core dissolvent.

Losses of uranium, thorium, and plutonium immediately upon decladding (3 hr) were 0.77, 0.51, and 0.53 per cent, respectively. The magnitudes of these values are probably related to the low density, the high oxygen-to-uranium ratio, and, most of all, to the observed core shattering. There was apparently essentially no change after 6 hr. However, these 6-hr values may be low since solution concentration at this time was very high and there is some suspicion that part of the uranium, thorium, and plutonium may have been carried down by solid ferrous sulfate. After 8 hr, thorium loss was over 1 per cent, and uranium and plutonium losses were approximately 2 per cent.

The surface of Pin A-117, used in the second run (Run S-2), appeared under the stereomicroscope to be noticeably less bright than Pin A-103. This pin was passive, and there was no attack by boiling 6 M H₂SO₄ in 1 hr. After the addition of formic acid (to 0.1 M concentration) failed to break the passivation, the 6 M acid was withdrawn and replaced by 8 M H₂SO₄. This appeared to attack the cladding upon reaching the boiling point. The cladding solution was sampled after 3 hr and withdrawn after 6 hr, at which time it was discovered that depassivation had not been complete or else passivation had recurred. Although about one-half of the stainless steel had been dissolved, the pin was still intact. Decladding was continued the following day with fresh 8 M H₂SO₄. The pin was still passive to boiling 8 M H₂SO₄, but passivation was readily broken by touching the pin with a steel rod, after which attack was vigorous. This cladding solution, withdrawn after 3 hr, removed the balance of the cladding, including end plugs. After completion of washing, the undissolved core residue (42.2 g recovered) was removed for later continuation of the core dissolution.

This was the only pin of the four dissolved by the Sulfex process which was passive. In the absence of any evidence of greater nitrate contamination in this run than in any of the others, the observed passivity is attributed more to the characteristics of its oxidized surface and to its previous history.

Shattering of core pellets was again observed in this run. Plugging of the capillary liquid-transfer line by small fragments of core was a major problem during filtration of the cladding solution.

Indicated losses of uranium, thorium, and plutonium at 3 hr were 0.26, 0.12, and 0.17 per cent. Although the pin was still in one piece after 6 hr, the cladding had evidently lost its integrity sufficiently in 3 hr to permit some attack of the core.

Thorium loss increased to 0.70 per cent, and uranium and plutonium losses to 1.6 and 1.8 per cent, respectively, after 6 hr. In the subsequent 3-hr attack by the fresh charge of 8 M H_2SO_4 , another 1.4, 0.57, and 1.1 per cent, respectively, of the uranium, thorium, and plutonium were lost. As in the first experiment, core shattering probably had an important bearing on the magnitude of these losses.

The core material was later returned to the dissolver and digested with 155 ml of 13 M HNO_3 core dissolvent for 5 hr. Upon withdrawal of the core solution it was discovered that the core pellets were covered with a white coating, presumably thorium sulfate. Dissolution was markedly suppressed, only about 75 per cent of the core being dissolved, instead of the usual 90 + per cent. The dissolver and core pellets had not been washed after decladding other than with the standard 100 ml of water. Evidently this is insufficient to satisfactorily eliminate sulfate contamination. Sulfate analyses indicate that initial sulfate concentration was about 0.15 M while in other experiments this was less than 0.02 M. Approximately 50 ml of water was added to the dissolver, and the core pellets were digested for 3 hr, which dissolved the white coating. Dissolution proceeded satisfactorily with a fresh 155-ml charge of core dissolvent, and was complete in 5 hr. Sulfate concentration in the second pass is calculated to have been about 0.06 M.

Pin A-108 also appeared to have a generally dull surface, but passivation was absent in this experiment (Run S-3). The cladding solution was sampled after 3 hr and withdrawn and filtered after 6 hr. All of the declad core pellets appeared to be entirely intact, and there were no indications of shattering.

Freedom from shattering was also indicated by the low uranium, thorium, and plutonium losses after decladding (3 hr): about 0.12, 0.07, and 0.12 per cent, respectively. These increased to 0.30, 0.12, and 0.33 per cent after an additional 3-hr contact with the boiling cladding solution.

To prevent a recurrence of the sulfate inhibition of core dissolution, as in the previous run, the core pellets were soaked overnight in 100 ml of water. With this additional washing, no difficulties with sulfate were encountered, and approximately 95 per cent of the core was dissolved in the first pass and the balance in the second.

Passivation was also absent in the decladding of Pin A-196 (Run S-4). Plugging of the stopcock in the line leading to the filter with a small fragment of cladding or core material during sampling necessitated taking of the 3-hr sample directly from the dissolver without filtering. The stoppage was cleared later, and the cladding solution was withdrawn and filtered after 6 hr.

Uranium, thorium, and plutonium losses after 3 hr were about 0.21, 0.10, and 0.14 per cent, respectively. In all three cases losses increased markedly to 1.6, 0.81, and 1.9 per cent at 6 hr. This rapid increase is probably indicative of shattering, although none had been apparent.

Analytical data for both the Sulfex and Darex experiments are shown in Tables 3 and 4. Material balances calculated from these data are not highly accurate, due primarily to the inherent difficulties in handling and measuring small volumes of concentrated solutions remotely. This was especially true of the composite core solutions.

TABLE 3. ANALYSES OF CLADDING SOLUTIONS FROM SULFEX DISSOLUTIONS OF IRRADIATED CONSOLIDATED EDISON FUEL PINS

Cladding Solutions														
Run	Pin	Dissolution Time, hr	Uranium		Thorium		Plutonium		Iron Concentration, g per liter	Gross Solution Radioactivity		Original Weight of Pin, g	End-Plug Residue, g	Remarks
			Concentration,	Loss ^(a) ,	Concentration,	Loss ^(a) ,	Concentration,	Loss,		Beta,	Gamma,			
			g per liter	per cent	g per liter	per cent	mg per liter	per cent		10 ⁸ cpm per ml	10 ⁹ cpm per ml			
S-1	A-103	3	0.089	0.77	1.26	0.51	0.14	~0.53 ^(b)	42.3	--	--	70.73		Severe shattering
		6	0.080	0.69	1.05	0.43	0.21	~0.80 ^(b)	34.6	--	--			
		8	0.119	1.8	1.66	1.2	0.30	~2.0 ^(b)	42.0	--	--	6.36		
S-2	A-117	3	0.020	0.26	0.20	0.12	0.030	0.17 ^(b)	25.4	--	--	69.31		Passivated, 8 M H ₂ SO ₄ used Pin still parti- ally clad
		6	0.082	1.6	0.73	0.70	0.22	1.8 ^(b)	18.1	--	--			
		3	0.073	1.4	0.65	0.57	0.13	1.1 ^(b)	20.8	--	--	Nil	Fresh charge 8 M H ₂ SO ₄ ; shattering	
S-3	A-108	3	0.0089	0.12	0.11	0.068	0.019	0.12	49.8	4.9	1.46	70.36		Shattering not observed
		6	0.017	0.30	0.14	0.12	0.040	0.33	40.2	4.6	1.13	4.29		
S-4	A-196	3 ^(c)	0.0161	0.21	0.15	0.095	0.033	0.14	54.0	4.1	1.96	70.65		Shattering not observed
		6	0.092	1.6	0.95	0.81	0.33	1.9	46.4	4.9	1.20	1.51		

(a) Based on an input of 1.75 g of uranium and 37.0 g of thorium.

(b) Based on an estimated input of 4.0 mg of plutonium.

(c) Sample taken directly from dissolver; all other samples filtered and withdrawn from the product receiver.

TABLE 4. ANALYSES OF CORE SOLUTIONS FROM SULFEX DISSOLUTIONS OF

Run	Solution	Volume, ml	Uranium		Thorium		Plutonium	
			Concentration, g per liter	Weight, g	Concentration, g per liter	Weight, g	Concentration, g per liter	Weight, g
S-1 ^(a)	First core	85	6.1	0.52	111	9.4	0.0159	0.0014
	Second core	50	--	--	28.5	1.4	0.0047	0.0002
	Composite ^(b)	--	--	--	--	--	--	--
S-2	First core	140	8.7	1.22	137	19.2	--	--
	First wash ^(c)	50	--	--	23	1.2	--	--
	Second core	150	2.5	0.37	54	8.1	--	--
	Second wash	50	--	--	--	--	--	--
	Second composite	200	--	--	37	--	0.0041	0.00082
S-3	First core	145	--	--	252	36.6	--	--
	Second core	50	--	--	37	1.9	--	--
	Composite	245	6.4	1.56	120	29.8	0.0149	0.0037
S-4	First core	145	--	--	230	33.2	--	--
	Second core	65	--	--	32	2.1	--	--
	Composite	250	6.5	1.62	123	30.8	0.0222	0.0056

(a) Dissolver fractured at start of core dissolution; dissolution continued with 12.6 g of recovered core material.

(b) Sample lost.

(c) Wash to remove thorium sulfate coating from core pellets.

IRRADIATED CONSOLIDATED EDISON FUEL PINS

Iron Concentration, g per liter	Sulfate Concentration, g per liter	Free Acidity, N	Gross Solution Radioactivity		Burnup	
			Beta, 10 ⁹ cpm per ml	Gamma, 10 ⁹ cpm per ml	Uranium, a/c	Core, MWD/T
0.21	2.9	--	--	--	0.46	~ 195
--	2.6	--	--	--		
--	--	--	--	--		
0.17	3.4	--	--	--		
0.14	2.1	--	--	--		
--	5.9	--	--	--	~ 0.47	~ 200
--	1.0	--	--	--		
0.02	--	8.3	--	--		
--	1.2	--	3.38	1.96		
--	1.2	--	0.52	0.64		
0.26	1.1	7.5	1.58	1.80	0.42	~ 175
--	1.6	--	5.14	2.87		
--	1.7	--	3.70	0.79		
0.11	1.5	7.6	3.02	2.75	0.70	~ 300

These were inescapably only approximate, and more reliance should probably be placed on calculated composite values based on the analyses of the individual solutions.

No indication of significant selectivity of dissolution among uranium, thorium, or plutonium is apparent in these results. Losses of all three were roughly comparable at a given time, and all increased at approximately the same rate with increasing contact time.

Plutonium analyses were made on aliquots of thenoyltrifluoroacetone extracts of the cladding solutions. Recovery of the analytical method was checked by one experiment in which duplicate samples of a simulated Sulfex cladding solution (stainless steel only) was spiked (using an aliquot of the plutonium extract from a core-solution analysis) at the level of a typical cladding solution, and carried through the standard procedure. Recovery of plutonium was 99 ± 2 per cent, indicating good reliability for the method.

Neither weights nor analytical data were obtained on the acid-insoluble residues retained by the filter in the experiments with irradiated pins. The residues retained were judged visually to be comparable with those resulting from the unirradiated specimens, and losses of uranium, thorium, and plutonium were estimated to be insignificant.

Darex Process

Two irradiated prototype Consolidated Edison fuel pins were dissolved by the Darex process, under the same conditions used for the unirradiated specimens.

As in the Sulfex experiments, the de-jacketed core pellets were refluxed with the cladding solution for an additional 3 hr to investigate the effect of prolonged contact on losses of fuel materials to the cladding solution. To eliminate any danger of sample contamination by possible traces of core solution held up in the apparatus from previous experiments, the cladding-solution sampling procedure was modified beginning with the Darex dissolutions. Formerly, samples were filtered through the same glass-frit filter used for the main cladding and core solutions and withdrawn from the product receiver, presenting possibilities of contamination. Cladding-solution samples for these runs were withdrawn directly from the dissolver with a pipette. All were, therefore, unfiltered and on an undiluted basis.

In the first Darex dissolution (Run D-5) Pin A-42 was introduced into warm de-cladding solution, and attack was immediate. After 1 hr, two 10-ml samples were withdrawn from the dissolver. Similar samples were taken at 4 hr, after which the cladding solution was withdrawn and discarded.

In washing the apparatus prior to the core dissolution, it was observed that there was a slight accumulation of a brown earthy-looking residue in the filter (estimated to be perhaps 1 to 3 g) which appeared to be finely divided core fragments. To dissolve this residue part of the core solvent was allowed to stand in the filter overnight. Also, portions of the boiling core solvent were occasionally circulated through the filter during core dissolution. This treatment appeared to dissolve the residue, and none was observed in the filter at the conclusion of the run.

No difficulties were encountered in the second Darex dissolution (Run D-6). By visual examination, the de jacketed pellets were entirely whole, and shattering appeared to be completely absent. This is borne out by the analytical results of the Darex experiments, shown in Tables 5 and 6. Uranium, plutonium, and thorium losses to the cladding solution approximately doubled with 3-hr additional contact. However, in Run D-5, total losses after 4 hr were in the 2.5 to 4.5 per cent range, while in Run D-6 losses were only 0.06 to 0.15 per cent. A comparison of Sulfex versus Darex losses on the basis of these data is difficult. Run D-5 had higher losses than any Sulfex run, whereas Run D-6 had lower losses than any observed in the Sulfex dissolutions. The extent of shattering of the core pellets appears to be a more significant variable than the nature of the dissolvent.

Activities of Darex solutions were studied in a little more detail than were those from the Sulfex tests. In addition to the usual gross beta and gross gamma determinations, the Darex solutions were also analyzed by gamma-ray spectroscopy. These data indicated that the gamma-activity of the cladding solutions, which was, after approximately 9 months of cooling, at nearly the same level as that of the core solutions, could be attributed principally to induced activity from the stainless steel. Most of it appeared to be due to cobalt-60 possibly in combination with some iron-59. No significant zirconium-95 and niobium-95 peaks were observed, even in Run D-5 cladding solutions, which contained from 1 to 3 per cent of the core. Gamma spectroscopy of the core solutions showed strong peaks from zirconium-95 and niobium-95 and possibly protactinium-233, in addition to those normally associated with thorium and uranium. More positive identifications would be possible if radiochemical analyses were performed on these materials.

Dissolution of Insulating Materials

All of the prototype Consolidated Edison fuel pins examined to date have contained end pellets of some ceramic material. Those from ORNL had end pellets of Kaowool. No quantitative data were obtained on the rate of dissolution of these Kaowool end pellets, although it was obvious that they were being attacked only slowly. Other ceramics, including Al_2O_3 , ZrO_2 , and MgO have also been proposed. Data have been presented⁽⁴⁾ which indicate that rates of dissolution of Al_2O_3 and ZrO_2 may be low.

In connection with other work at Battelle, additional data have been obtained on the resistance of irradiated Al_2O_3 to chemical attack. One Al_2O_3 end-plug specimen from a prototype Consolidated Edison fuel pin irradiated 2 cycles at the MTR (~4000 MWD/T) was found to have lost <1 per cent of its weight after about 20-hr exposure to a variety of concentrated solvents, including nitric acid containing from 0.04 to 1 M fluoride ion. Another approximately 1 per cent was dissolved after an additional 26-hr digestion in refluxing 13 M core dissolvent.

These data suggest that the chances of removing Al_2O_3 end pellets chemically are remote, and that occasional mechanical removal from the dissolver would be necessary if this material is selected to thermally insulate the ends of Consolidated Edison fuel pins.

TABLE 5. ANALYSES OF CLADDING SOLUTIONS FROM DAREX DISSOLUTIONS OF

Run	Pin	Dissolution Time, hr	Cladding Solutions			
			Uranium		Thorium	
			Concentration, g per liter	Loss ^(a) , per cent	Concentration, g per liter	Loss ^(a) , per cent
D-5	A-42	1	0.089	2.1	1.0	1.1
		4	0.163	3.7	2.4	2.6
D-6	A-115	1	0.0026	0.063	0.028	0.032
		4	0.0065	0.15	0.053	0.057

(a) Based on an input of 1.75 g of uranium and 37.0 g of thorium.

TABLE 6. ANALYSES OF CORE SOLUTIONS FROM DAREX DISSOLUTIONS OF

Run	Solution	Volume, ml	Uranium		Thorium	
			Concentration, g per liter	Weight, g	Concentration, g per liter	Weight, g
D-5	First core	145	11.9	1.73	231	33.4
	Second core	55	1.82	0.09	26.3	1.5
	Composite	250	6.62	--	147.5	--
D-6	First core	165	10.6	1.75	187.5	30.8
	Second core	50	1.74	0.08	25.0	1.3
	Composite	260	7.15	--	130.0	--

IRRADIATED CONSOLIDATED EDISON FUEL PINS

Plutonium		Iron Concentration, g per liter	Gross Solution Radioactivity		Original Weight of Pin, g	Remarks
Concentration, mg per liter	Loss, per cent		Beta, 10^8 cpm per ml	Gamma, 10^9 cpm per ml		
0.245	2.4	38.5	4.4	1.08	70.35	Marked shattering; fines observed in filter
0.460	4.5	42.0	4.2	1.11		
0.045	0.31?	38.5	3.7	1.03	69.40	All pellets intact
0.0123	0.08	37.0	3.9	0.99		

IRRADIATED CONSOLIDATED EDISON FUEL PINS

Core Solutions		Iron Concentration, g per liter	Free Acidity, N	Gross Solution Radioactivity		Burnup	
Plutonium Concentration, g per liter	Weight, g			Beta, 10^9 cpm per ml	Gamma, 10^9 cpm per ml	Uranium, a/o	Core, MWD/T
--	--	--	--	3.64	3.19		
--	--	--	--	0.56	0.60		
0.0174	0.0043	0.21	7.1	2.06	3.24	0.45	~ 190
--	--	0.34	--	3.18	2.82	0.66	
--	--	0.08	--	0.75	0.98	0.60	
0.0238	0.0062	0.25	8.1	2.84	2.79	0.65	~ 275

CONCLUSIONS

The only effect of irradiation of Consolidated Edison power-reactor fuel of importance to its dissolution by the Sulfex or Darex processes which was noted in this investigation was shattering of the core pellets. This is, however, an irradiation effect of major significance, since losses of fissile and fertile materials to decladding solutions appear to depend more upon the extent of shattering than upon any other variable. In the absence of shattering, losses of uranium, thorium, and plutonium of less than 0.1 per cent each were readily attained. With shattered pins these losses were higher by an order of magnitude or more.

The data do not permit a correlation of the extent of irradiation exposure with shattering because shattering of core pellets was observed randomly over the entire range of burnups covered by the samples studied (~175 to ~300 MWD/T core). There was also no indication of a threshold burnup above which shattering occurred. Some pellets irradiated to 175 MWD/T shattered, but some irradiated to 300 MWD/T did not.

Losses of fuel values to the cladding solution appeared to be no greater with the Darex than with the Sulfex process. Cross contamination between decladding and core dissolution was a considerable problem with the Sulfex process. The Darex process appeared to be free of this problem and is favored for this reason. Objections to the larger volume of Darex cladding waste solutions do not appear to be insurmountable. Some of the data indicate that it may be possible to reduce this to at least the volume of Sulfex waste, and further study of this possibility is recommended in view of the other attractive features of Darex decladding.

No effects of irradiation upon core-dissolution rates were apparent at the irradiation levels tested.

It should be noted that the prototype Consolidated Edison core material investigated during this program departed somewhat from that to be ultimately used. Density was lower, ~85 per cent, instead of 94 to 95 per cent of theoretical. The cores were air-fired, and the oxygen-to-uranium ratio approached that for U_3O_8 rather than the proposed UO_2 . It would be expected that losses to the decladding solution would be lower with core material having a high density and a low oxygen-to-uranium ratio. Core-dissolution time would be expected to be longer.

REFERENCES

- (1) Culler, F. L., and Blanco, R. E., "Dissolution and Feed Preparation for Aqueous Radiochemical Separations Processes", Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Paper No. P/1930 (1958).
- (2) Bruce, F. R., Blanco, R. E., and Breese, J. C., "Recent Developments in Feed Preparation and Solvent Extraction", Fifth Nuclear Congress, Cleveland, Ohio, April 7, 1959, ORNL-CF-11-91 (March 20, 1959).
- (3) Blanco, R. E., Ferris, L. M., Flanary, J. R., Kitts, F. G., Rainey, R. H., and Roberts, J. T., "Chemical Processing of Power and Research Reactor Fuels at

Oak Ridge National Laboratory", Proceedings of the AEC Symposium for Chemical Processing of Irradiated Fuels, Richland, Washington, TID-7583 (October 20-21, 1959).

- (4) Ferris, L. M., and Kibbey, A. H., "Laboratory Development of the Sulfex Process for the Dissolution of Consolidated Edison Power Reactor Fuel", ORNL-2714 (November 2, 1959).
- (5) Private communication from L. M. Ferris (January 5, 1960).