ORNL-2461
Chemistry-Separation Processes
for Plutonium and Uranium

DEVELOPMENT OF THE SULFEX PROCESS FOR DECLADDING STAINLESS-STEEL-CLAD POWER REACTOR FUEL ELEMENTS WITH SULFURIC ACID

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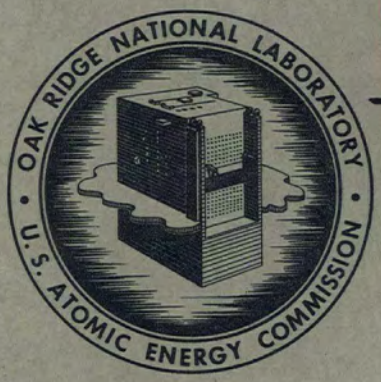

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Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

ORNL-2461

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

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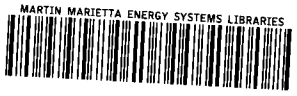

ABSTRACT

A flowsheet, based on laboratory studies, was designed for processing the fuel proposed for the Yankee Atomic Power Reactor by the Sulfex process. This process consists of selective dissolution of the stainless steel cladding by sulfuric acid, with subsequent dissolution of the exposed UO_2 core in nitric acid. With appropriate modifications, the process should be applicable to other stainless steel-clad reactor fuels.

With unirradiated fuel specimens, dissolution of type 304L stainless steel cladding proceeded at rates of 2-5 $mg/cm^2/min$ in boiling 4 M H_2SO_4; the rate appeared somewhat lower with irradiated specimens. From 0.01 to 0.02% of the uranium was lost to the decladding solution. The spent decladding solution may be neutralized with lime to form a plasterlike solid waste; open-pit disposal of this waste appears feasible. Subsequent dissolution of the UO_2 core proceeded readily in nitric acid, yielding a concentrated uranyl nitrate solution which may be readily processed in existing Purex solvent extraction facilities.

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1.0 INTRODUCTION

Optimum conditions were determined for the Sulfex process for selective dissolution of the stainless steel cladding from power reactor fuel elements by sulfuric acid, with subsequent dissolution of the UO_2 core in nitric acid for solvent extraction processing.

Stainless-steel-jacket fuel elements, which permit the use of higher reactor operating temperatures and better heat transfer mediums than are possible with aluminum-clad fuel elements, present a formidable chemical processing problem in that the stainless steel is passive in the conventional fuel dissolvent, nitric acid. The use of the halogen acids or halogen additions to nitric acid poses a problem in materials of construction for process equipment. Selective dissolution of the stainless steel, without attack on the core materials, permits the core to be dissolved in nitric acid, yielding an aqueous solution best suited for solvent extraction in existing tributyl phosphate systems, and would decrease the volume of highly radioactive wastes that must be stored indefinitely. As a result of the experiments, a flowsheet which applies specifically to the fuel proposed for the Yankee Atomic Reactor was designed; with modifications the process should be applicable to other stainless-steel-clad reactor fuels. However, pending further tests, use of this process for decladding APPR fuels must remain in doubt. High uranium losses, perhaps due to oxidation of UO_2 during long storage, were observed.

Previous work, principally at KAPL, on processing fuels with sulfuric acid was designed to dissolve the stainless steel jackets of a particular fuel in sulfuric acid; nitric acid was added to the residual solution to dissolve the core.[1,14] Separation of jacket and core was not intended. Laboratory studies at ORNL have been based upon such a separation. Much of the development work reported here has been previously reported in Chemical Technology Division monthly progress reports for May through December 1957,[3-10] and in ORNL Central Files memorandums.[2,11-13,15,16]

Advantages of a selective dissolution process, such as the Sulfex process, for the removal of stainless steel cladding from power reactor fuel include a greatly reduced volume of radioactive waste for permanent storage by elimination of relatively insoluble stainless steel salts from the solvent extraction waste streams; provision of nitric acid-salted, concentrated uranium feed, free of deleterious sulfates or halogens, for solvent extraction; and the possibility of a relatively modest capital investment in dissolution-feed preparation equipment (as indicated by initial cost estimates) compared to the complex and costly outlay of equipment required for the Darex head-end process.[13] In the Darex process, currently being developed at ORNL, integral dissolution of stainless steel--clad fuel such as the APPR or Yankee Atomic is accomplished with dilute aqua regia. Chloride is nearly quantitatively removed from the dissolver product solution by oxidative distillation,

prior to final feed adjustment for solvent extraction. Titanium equipment is needed to withstand the severely corrosive conditions.

The authors acknowledge the assistance of the laboratory technicians who conducted many of the experiments reported here: L. A. Byrd, R. C. Shipwash, and J. F. Talley; and also the valuable assistance of G. R. Wilson, W. L. Laing, C. E. Lamb, E. I. Wyatt, and U. Koskela of the ORNL Analytical Chemistry Division.

2.0 CHEMICAL FLOWSHEET

The proposed flowsheet for the Sulfex process as applied to spent fuel from the Yankee Atomic Power Reactor (Fig. 1) provides for dissolution of the cladding in 200% excess of boiling 4 M H_2SO_4; the spent decladding solution is sent to waste disposal. Dissolution of the exposed UO_2 core with 8 M HNO_3 provides, after suitable adjustment, a feed solution for subsequent processing by solvent extraction. The Yankee Atomic fuel assembly has a core of sintered UO_2 pellets weighing 362 kg (319 kg of uranium). The core is encased in a jacket of type 304L stainless steel tubing, 0.336 in. o.d. and 15 mils wall thickness, weighing 69 kg including the end caps. The steel tie rods of the fuel assembly are mechanically removed before chemical processing is started. The end caps, 1 in. long by 0.335 in. dia, do not completely dissolve during the decladding step and the residue becomes passivated in the nitric acid subsequently used to dissolve the UO_2 core. The passivation may be broken by adding 400 g of steel shot with the decladding solution.

Based on one fuel assembly, a bundle of fuel rods weighing 431 kg is charged in batches to the dissolver, which contains 1742 liters of 4 M H_2SO_4 at 90-100°C and the residual end caps from the previous decladding-core dissolution cycle. The contents of the dissolver are refluxed at 107°C for 4 hr to complete the decladding. The spent decladding solution is drained from the dissolver, and the dissolver and contents are rinsed with water. The spent decladding solution and rinse are combined and sent to waste disposal. The volume of rinse depends on the dissolver design, but 50 liters is arbitrarily used in the preliminary flowsheet.

To the exposed core in the dissolver is added 727.6 liters of 8 M HNO_3; dissolution of UO_2 is complete at 105°C in 2 hr. The dissolver product solution is transferred to a digestion vessel for treatment to remove silica, an impurity deleterious to solvent extraction. The dissolver is rinsed with water and the rinse is combined with the dissolver product solution in the digestion vessel. After digestion to coagulate soluble silica, the dissolver product solution is clarified by centrifugation or filtration and then adjusted to the appropriate feed composition for solvent extraction.

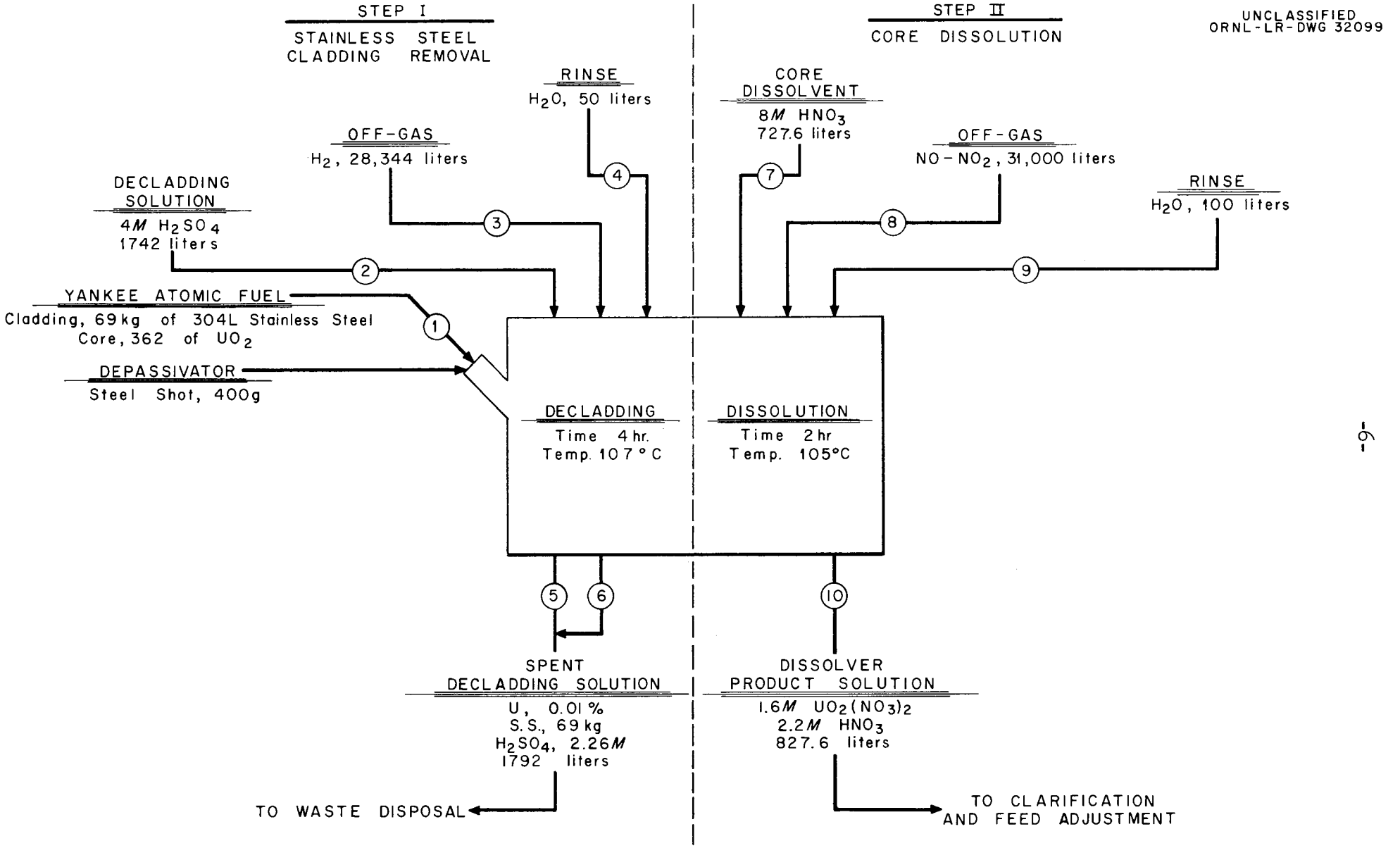

Fig. 1 Schematic Flowsheet for Sulfex Process Applied To Yankee Atomic Reactor Fuel (Number streams refer to Appendix 2)

3.0 DISSOLUTION STUDIES

Fuel elements and assemblies that have been designed and fabricated for existing and proposed power reactors may be broadly grouped, for chemical processing purposes, into two categories: the high-uranium-content fuels containing normal or slightly enriched uranium and the low-uranium-content fuels of highly enriched uranium. In the first category are those fuels with cores of sintered uranium dioxide pellets or rods of metallic uranium, and uranium alloyed with niobium or molybdenum. These core materials are sealed in tubes of stainless steel, a structural material desirable for its ease of fabrication, thermal stability, resistance to corrosion, and neutron cross-section.

Removal of stainless steel cladding by selective dissolution appears promising. Initial development work with sulfuric acid as a selective dissolvent for stainless steel has been directed mainly to fuel elements designed for the Yankee Atomic Power reactor, i.e., sintered pellets of UO_2 canned in tubes of type 304L stainless steel (Appendix I). This particular fuel type will probably become a major fraction of the annual load of a large-capacity radiochemical processing plant serving commercial power reactors.

3.1 Dissolution of 304L Stainless Steel in Sulfuric Acid

Dissolution Rate. The dissolution rate of type 304L stainless steel in sulfuric acid was influenced largely by the acid concentration and the temperature at which the reaction was initiated. The rate increased from 2 to 6 mg/cm^2/min when the sulfuric acid concentration was increased from 2 to 8 M (Table 1). The 2-min dissolution rates for stainless steel extrapolated to 2 hr, which would represent 100% dissolution of the specimens, indicated a penetration rate of 8 to 14 mils/hr in 4 and 6 M H_2SO_4, respectively. In longer tests with 4 M H_2SO_4 preheated to boiling before insertion of the specimen, the rate was relatively constant at about 14 mils/hr* (Fig. 2).

Solubility. The solubility of 304L stainless steel decreased very linearly from 43 mg/ml in 2 M H_2SO_4 to about 8 mg/ml in 8 M H_2SO_4 at 100 to 130°C (Fig. 3). It is noted, however, that the dissolution rate is apparently quite slow at acid concentrations below 4 M (Table 1). Therefore, 4 M H_2SO_4 was chosen for the decladding solution since it represented the best compromise between dissolution rate and solubility. As the 4 M H_2SO_4 became saturated with stainless steel (105-110°C), the free acidity decreased to ~ 2 M and the solution contained 100--110 g of stainless steel per liter before precipitation occurred (Fig. 4). The dissolution rate remained fairly constant at 4 mg/cm^2/min until the precipitation started. These data were obtained by refluxing 4 M H_2SO_4 with excess stainless steel, sampling the resulting solution periodically, and analyzing for dissolved stainless steel and free acid.

*A dissolution rate of 1 mg/cm^2/min is equivalent to ~ 3 mils/hr penetration rate.

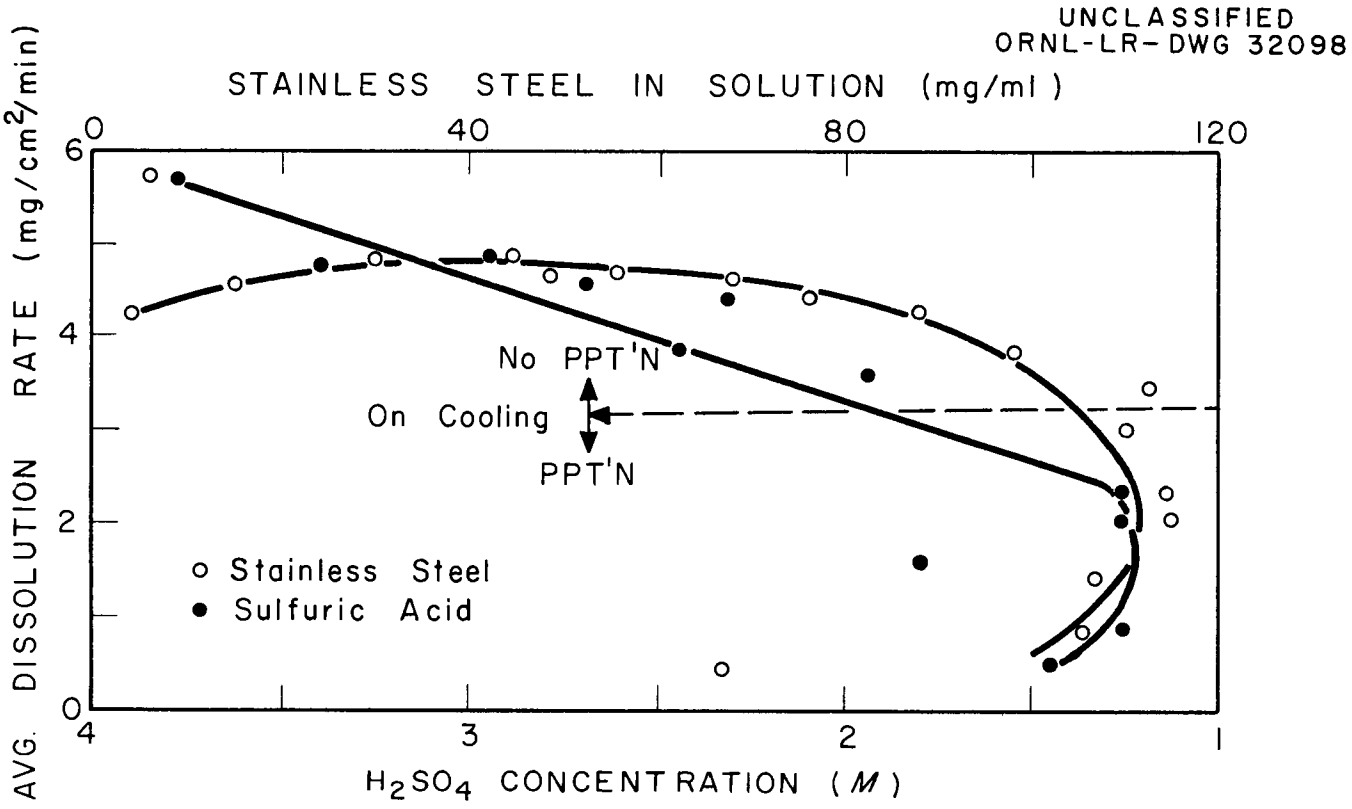

Fig. 2 Average Dissolution Rate of Type 304L Stainless Steel During Saturation of $4M$ H_2SO_4

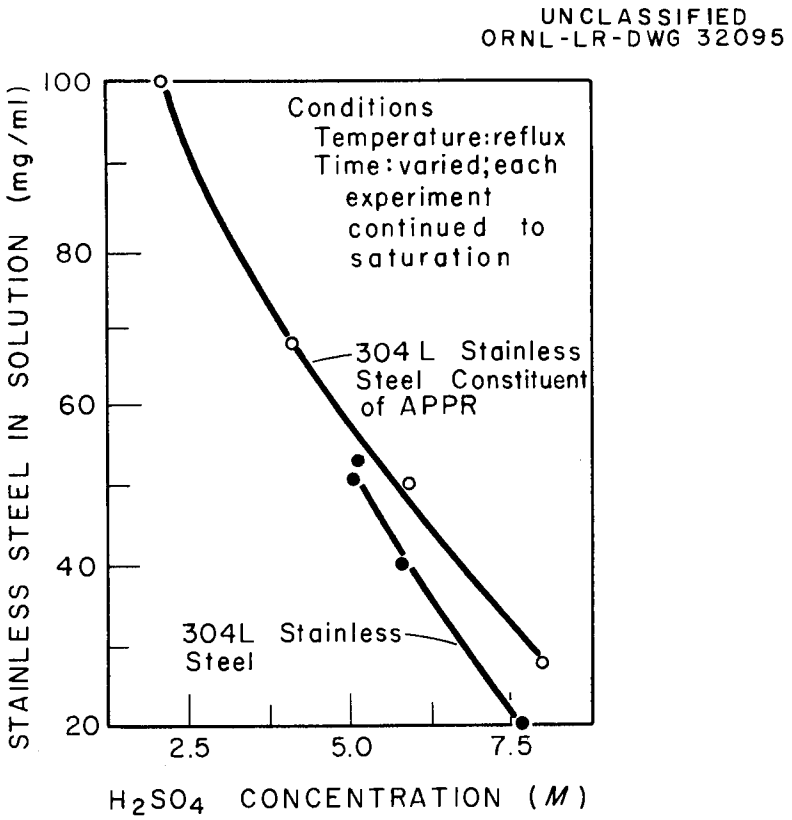

Fig. 3 Solubility of Stainless Steel in Sulfuric Acid

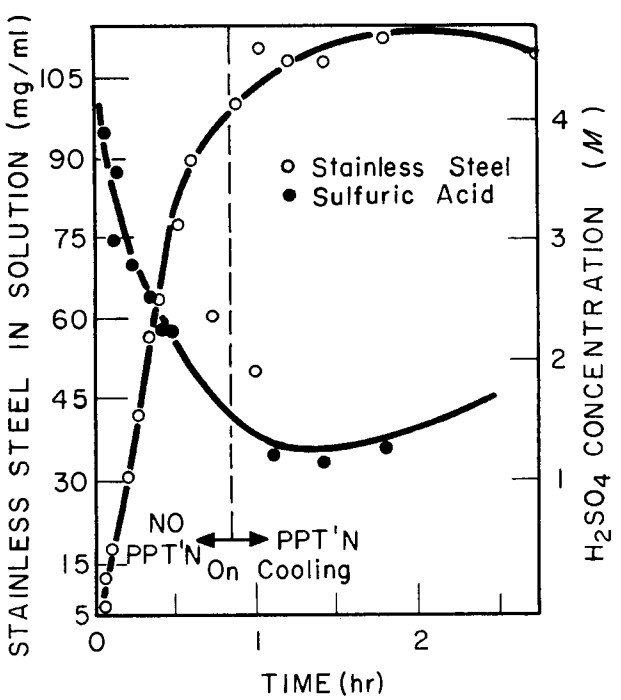

Fig. 4 Variation of Acid and Stainless Steel Concentrations During Saturation of 4*M* H_2SO_4

Table 1. Dissolution Rates and Solubilities of Unirradiated Cladding and Core Materials in Sulfuric Acid

Dissolution time: 2 min
Temperature: boiling

Material	Dissolution Rate ($mg/cm^2/min$)			
	2 M H_2SO_4	4 M H_2SO_4	6 M H_2SO_4	8 M H_2SO_4
304 L stainless steel	---	2.27	4.66	5.78
UO_2	Neg	0.0015	0.0016	Neg
U metal	0.092	0.119	0.089	0.093
U-10% Mo	1.34	1.40	1.41	2.16
U-10% Nb	Neg	Neg	Neg	Neg

Table 2. Sulfuric Acid Consumption During Dissolution of Stainless Steel

Expt. No.	Stainless Steel Dissolved		Sulfuric Acid Consumed	
	(g)	(M)*	(M)	(M/mole SS)
1	26.9	0.48	0.88	1.81
2	28.5	0.51	0.92	1.79
3	28.7	0.52	0.99	1.92
4	28.5	0.51	0.82	1.60
5	27.9	0.50	0.95	1.87
6	28.5	0.51	1.07	2.09
7	28.6	0.52	1.08	2.09
8	28.5	0.51	0.93	1.81
			avg.	1.87

*Based on assumed molecular wt for stainless steel of 55.5.

Table 3. Solubilities of Cladding and Core Materials

Dissolution time: 2.5 hr
Temperature: reflux
Results calculated from analyses of solutions after cooling to room temperature

Material	Amount Dissolved[a]							
	2 M H_2SO_4		4 M H_2SO_4		6 M H_2SO_4		8 M H_2SO_4	
	(mg/ml)	(% of Total)	(mg/ml)	(% of Total)	(mg/ml)	(% of Total)	(mg/ml)	(% of Total)
304L stainless steel	43.0		47.1		44.8		7.9	
304L stainless steel from APPR fuel	101		67.3		49.7		28.9	
UO_2	0.023		0.066	0.06	0.153	0.11	0.420	0.24
U metal	0.027		0.084	0.58	0.284	0.92	0.690	1.44
U-10% Mo	0.068		0.039	0.07	0.065	0.12	0.182	0.32
U-10% Nb	0.0009		0.0007	Neg	0.007	0.01	0.005	

[a] Values for core materials given for uranium.

Sulfuric Acid Consumption. From the results of several individual determinations (Table 2) the average consumption of sulfuric acid during complete dissolution of 304L stainless steel was found to be 1.87 moles per mole of the alloy. The "molecular weight" of 304L stainless steel was estimated as 55.5. Weighed specimens of the alloy were dissolved in excess sulfuric acid of known volume and concentration. After dissolution, the solutions were analyzed for free acid, and the acid consumption was computed by difference.

Passivation of Stainless Steel. When partially saturated sulfuric acid was recycled to fresh stainless steel specimens, the metal surface invariably became passivated; this phenomenon was never observed when fresh hot acid was added to fresh specimens. The well-known technique of touching the specimen with actively corroding iron (e.g., steel wool) was employed to break the passivation.

3.2 Dissolution of Core Material in Decladding Solution

Dissolution rates for the core materials of interest---UO_2, metallic uranium, and uranium alloyed with 10% niobium or with 10% molybdenum---were 2- to 2000-fold less rapid than those of 304L stainless steel (Table 1). After 2.5-hr reflux of these core materials in 4 M H_2SO_4, uranium concentrations in solution were less than 0.1 mg/ml (Table 3) representing less than 0.1% uranium loss for the UO_2 and the alloys. The per cent losses reported are not necessarily comparable to those that would be obtained in an actual process since the dissolution rate depends somewhat on the subdivision of the core material (Fig. 5).

3.3 Decladding of Whole Fuel Elements

The possibility of selectively dissolving the stainless steel constituent of the fuel assemblies from the Army Package Power Reactor (APPR) with sulfuric acid was briefly investigated. These fuel assemblies are made up of plates with a core of sintered UO_2 powder, highly enriched, intimately mixed with stainless steel powder and clad with stainless steel (Appendix 3).

3.3.1 Unirradiated Fuel Yankee Atomic Pins. The average dissolution rate of 304L stainless steel when individual unirradiated prototype Yankee Atomic fuel pins were declad with 3 M H_2SO_4 was too low for practical application (Table 4); passivation of the stainless steel halted the reaction. With 4 M H_2SO_4, a useful rate, about 2 mg/cm^2/min, was obtained with the initial temperature of the decladding solution at 95°C before the specimen was added. With 6 M acid, the average rate was about 5 mg/cm^2/min when the specimens were introduced into preheated solution. However, when the specimens were placed in the decladding solution at room temperature, and gradually heated to 95°C, the rate decreased to ~ 2 mg/cm^2/min (Fig. 6). In the chemical processing plant, therefore, it will be desirable to preheat the decladding solution before the fuel elements are charged to the dissolver, so that the decladding time may be minimized.

Table 4. Dissolution of Stainless Steel Cladding from Unirradiated Prototype Yankee Atomic Fuel with Sulfuric Acid

Prototype Fuel Specimens: Sintered UO_2 pellets (61 g) encased in tubes of type 304L stainless steel (28 g)

Dissolution of cladding carried to completion unless passivation occurred.

Initial temperature of decladding solution was 95°C, or at room temperature and heated gradually to 95°C after fuel specimen was added.

H_2SO_4 (M)	H_2SO_4 % Excess[a]	Initial Temp. (°C)	Avg. Diss. Rate ($mg/cm^2/min$)	U Loss (%)	Diss. Time (hr)	Stable Sol'n[b]
3.0	-26	95	0.49[c]	0.001	9	No
4.0	50	95	2.18	0.004	5	No
4.0	230	95	2.09	0.010	5	Yes
4.0	400	95	1.80	0.006	5	Yes
6.0	200	25	2.51	0.011	4	No
6.0	200	95	5.12	0.005	3	No
6.0	300	25	1.81	0.008	5	No
6.0	300	95	6.16	0.008	1.5	No
6.0	400	25	1.83	0.009	5	Yes
6.0	400	95	4.79	0.009	3	No
6.0	500	25	2.02	0.005	4	Yes

[a] Based on 2 mols of H_2SO_4/mol (assumed to be 55.5 g) of stainless steel.

[b] After cooling and standing for several days, spent decladding solution remained stable, i.e., no evidence of precipitation.

[c] Stainless steel passivated.

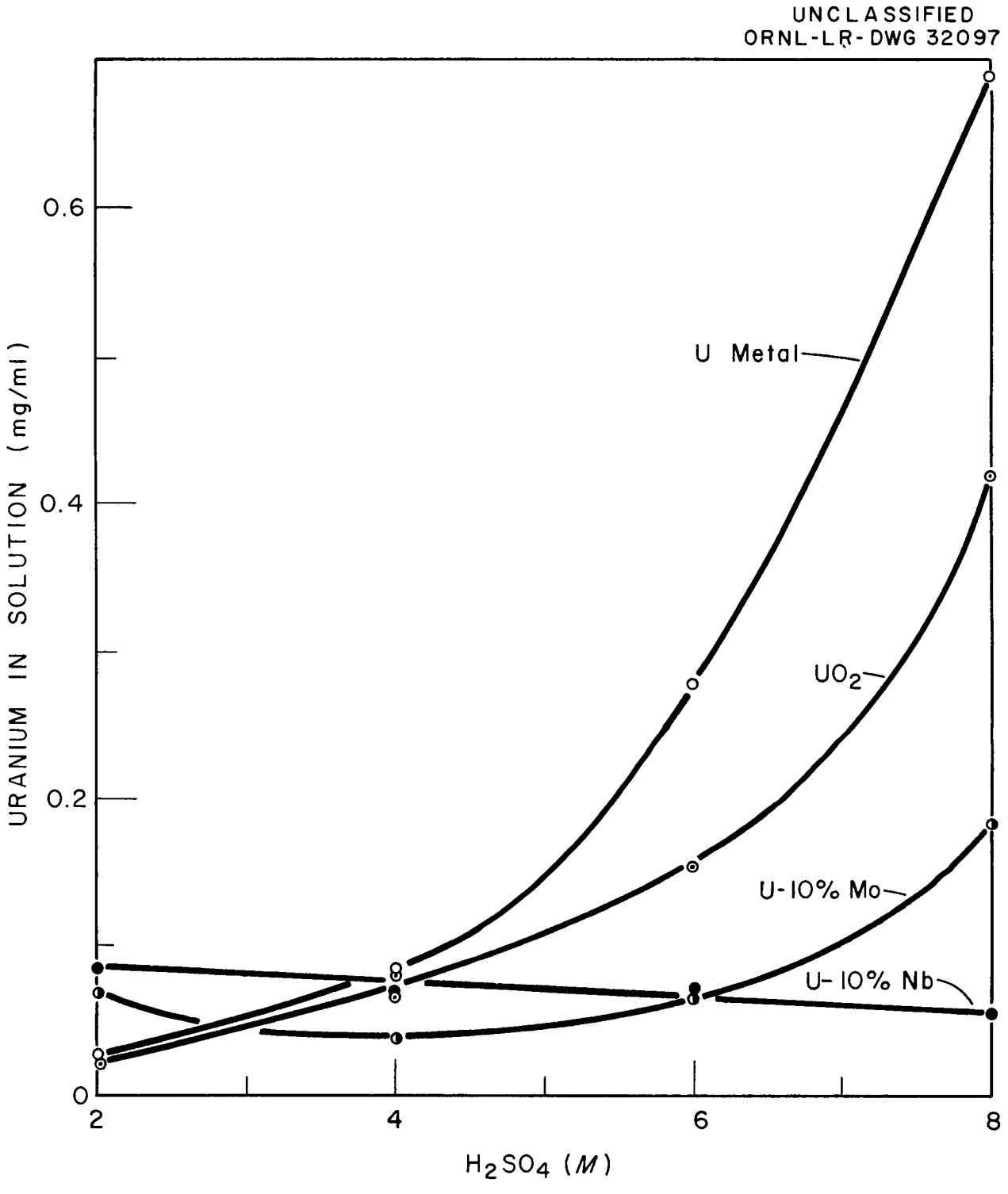

Fig. 5 Solubilities of Unirradiated Core Materials in Sulfuric Acid; Data taken from Table 3

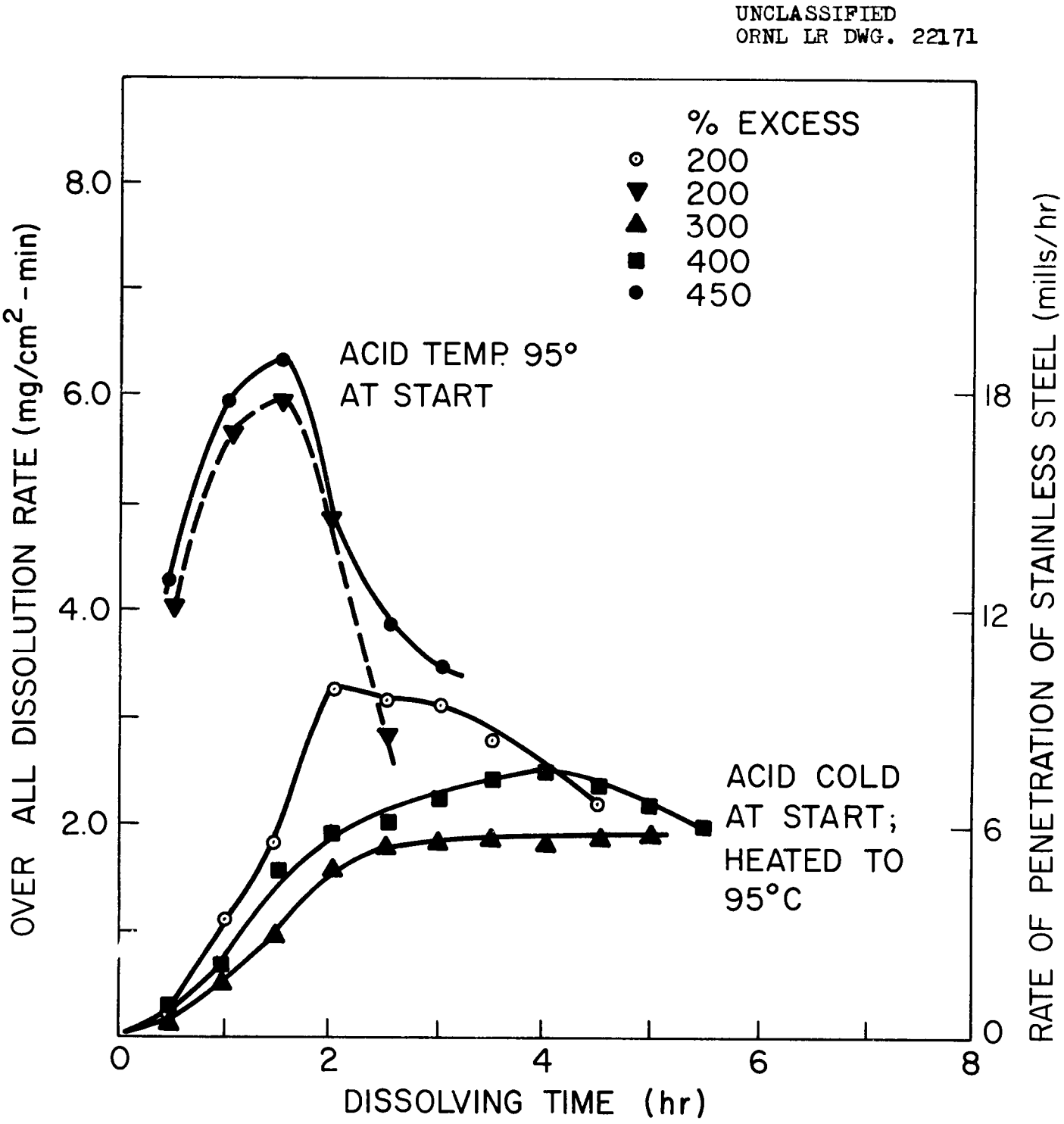

Fig. 6. Dissolution Rate of Stainless Steel Cladding of Yankee Atomic Power Reactor Fuels in ~ 6.6 *M* H_2SO_4.

Referring to Table 4 which contains data from individual decladding experiments with prototype Yankee Atomic fuel pins, the effect of sulfuric acid concentration on the stability, i.e., absence of precipitation from the spent decladding solution after several days storage at room temperature, may be observed. Starting with 4 M H_2SO_4 with 230% acid in excess of that required to dissolve the stainless steel, a spent decladding solution is produced which is stable. A 230% excess of sulfuric acid yields a spent decladding solution containing 44 g of stainless steel per liter. With 6 M H_2SO_4, 200% excess acid, precipitation occurred from the spent decladding solution with nearly the same concentration of dissolved stainless steel as produced in the former experiment. Starting with 6 M H_2SO_4, the spent decladding solution is metastable when 400% excess acid is used (34 g SS/liter), and becomes stable when 500% excess acid is used (28 g SS/liter).

From the results of those experiments, it was concluded that with 4 M H_2SO_4 a minimum 200% excess of acid should be used so that precipitation from the spent decladding solution in storage may be avoided.

APPR Fuel. A small specimen of APPR fuel, a section cut from one plate, was partially dissolved in 4 M H_2SO_4 with 400% excess acid preheated to 95°C. The average dissolution rate of the stainless steel portion of the specimen was 5.4 mg/cm^2/min, which is greater than twice the rate obtained with the prototype Yankee Atomic fuel pins under the same conditions. It is assumed that the state of subdivision, that is, the much larger surface area of stainless steel exposed in the APPR specimen, is responsible for the more rapid dissolution rate.

The dissolution of stainless steel was not as selective as desired; 0.31% of the uranium was found in the spent sulfuric acid solution. Again, the state of subdivision of the core may be responsible for this result. At any rate, a loss of enriched uranium of this magnitude could not be tolerated in the chemical processing plant. If this loss could not be reduced to a tolerable level, ~0.01% or less, a procedure would have to be developed to recover this uranium from the spent sulfuric acid solution before the solution is sent to permanent waste storage.

In the decladding experiments with prototype Yankee Atomic fuel pins, uranium losses were very modest, 0.004 to 0.011%. In this case, sintered, compacted pellets of UO_2 of minimum surface area are exposed to attack by sulfuric acid. In a processing plant, uranium loss as low as this is considered negligible.

Attempts to selectively dissolve the stainless steel in specimens of highly irradiated APPR fuel with sulfuric acid resulted in dissolution of nearly 95% of the UO_2 along with the stainless steel (Section 3.3). Consequently, it was suspected that the UO_2 in the APPR samples had been oxidized to U_3O_8, either during irradiation or while stored for decay of short-lived fission products. The specimens, cut from active plate sections, were exposed to air during several months storage. It was also thought that hydrogen peroxide might be formed in the solution by gamma radiation from the intensely radioactive specimens during dissolution.

It was decided to briefly examine the effect on uranium loss to the sulfuric acid dissolvent of several oxidants: hydrogen peroxide, dichromate, manganese dioxide, and chromic acid.

Addition of an arbitrarily chosen large excess of hydrogen peroxide to spent decladding solution in contact with UO_2 powder resulted in a uranium loss of 50% to the decladding solution. A 14.5-g specimen of

APPR fuel plate was dissolved in 6 M H_2SO_4, 700% excess, at 95°C which yielded a solution containing 0.052 mg of uranium per ml, 2.6% loss. After cooling to room temperature, the solution was made 0.5 M in H_2O_2, allowed to stand 3 hr, and heated again to 95°C to destroy the excess hydrogen peroxide. Analysis of this solution showed that the uranium concentration had increased to 1.38 mg/ml, representing 50% dissolution of the uranium.

Continuous addition of 3% hydrogen peroxide during dissolution of APPR specimens in boiling 4 M H_2SO_4 promoted 90 to 95% dissolution of the UO_2, while one initial addition to 0.5 M H_2O_2 increased the loss from 0.5% to 5%.

Specimens of APPR fuel plate were dissolved into 6 M H_2SO_4 at 95°C in the presence of 0, 0.005, and 0.05 M $Na_2Cr_2O_7$. The uranium concentrations of the resulting solutions were 0.007, 0.058, and 0.91 mg/ml, corresponding to 0.5, 3.8, and 69% dissolution of the uranium, respectively.

Table 5 summarizes the effect of manganese dioxide, chromic acid, and hydrogen peroxide on the dissolution of UO_2. In these experiments a calculated excess of oxidant was added during dissolution of APPR fuel specimens in boiling 4 M H_2SO_4; uranium dissolution varied from 66 to 90%.

Table 5. Effect of Oxidizing Agents on Dissolution of Unirradiated APPR Fuel Elements in Boiling 4 M H_2SO_4 (200% Excess)

Oxidant	Uranium Dissolved In H_2SO_4 (%)	Uranium Dissolved In 2 M HCl-5 M HNO_3 Wash (%)	Uranium Lost to Residue (HF wash) (%)	Uranium Material Balance (%)	Excess of Oxidant (%)
None	0.42		1.21		
H_2O_2	88.1	9.0	1.3	98.4	900, Based on UO_2
MnO_2	66.2	39.4	0.4	106.0	5, Based on UO_2
CrO_3	65.8	31.1	0.4	97.3	5, Based on UO_2 + Fe
CrO_3	88.2	9.4[a]	0.5	98.1	5, Based on UO_2 + Fe
CrO_3[b]	90.7	6.6	0.3	97.6	5, Based on UO_2 + Fe

[a] 8 M HNO_3 wash instead of dilute aqua regia.

[b] 400% excess H_2SO_4.

It is concluded that even small amounts of oxidizing agents greatly increase the dissolution of UO_2 by sulfuric acid such that selective dissolution of the stainless steel, as accomplished with the Yankee Atomic reactor fuel, may be impossible with the low-uranium-content fuels of the APPR type where UO_2 powder is intimately mixed with stainless steel. Total dissolution of this type of fuel with sulfuric acid is probably feasible under the proper conditions; however, solvent extraction of uranium with tributyl phosphate is inefficient with solutions of high sulfuric acid content and would require sulfuric acid-resistant equipment at least across the first cycle.

3.3.2 Irradiated Fuel

A number of experiments were run with irradiated prototype fuels to determine the effects of irradiation on dissolution rate and the behavior and distribution of gross and specific fission products and uranium and plutonium.

Prototype Yankee Atomic Fuel. Two prototype fuel specimens, each containing a sintered UO_2 pellet weighing about 6 g clad in 10 g of 304L stainless steel were irradiated for 60 hr in the ORNL Graphite reactor to a total of 0.4 Mwd/ton U. After 5 hr storage to permit decay of short-lived fission products, the pins were declad in 250 ml (200% excess) of refluxing 4 M H_2SO_4. The pins were refluxed for 21 hr to assure complete dissolution of the cladding. Dissolution rates were not obtained. Analyses showed uranium losses of 0.012 and 0.009% to the decladding solutions, which agree closely with loss data obtained with unirradiated Yankee Atomic fuel pins. Gamma spectra of the decladding solutions indicated that essentially all of the radioactivity was due to activated stainless steel components.

A prototype fuel pin, 44 g of UO_2 pellets clad in 22 g of 304L stainless steel was irradiated in the ORNL Low Intensity Training Reactor to the equivalent of 250 Mwd/T and "cooled" for 72 days. After 21-hr reflux in 130% excess of 4 M H_2SO_4, only 68% of the cladding had dissolved at an average rate of 0.42 $mg/cm^2/min$. It was decided that the 130% excess of acid was insufficient to maintain a practical dissolution rate.

Inspection of the remaining cladding showed it to be intact, and uniformly corroded. The partially spent decladding solution was discarded and replaced with 6 M H_2SO_4 (600% excess). The remainder of the cladding was removed in 6 hr at a rate of 1--2 $mg/cm^2/min$. Acid consumption was 1.89 mols per mol of stainless steel. Uranium and plutonium analyses of the spent decladding solution showed 0.0025 mg U/ml and 220 Pu alpha counts/min/ml, equivalent to losses of 0.02 and 0.06%, respectively. The spent decladding solution was extremely radioactive with activated stainless steel components (3.7×10^8 gamma counts/min/ml); a first approximation indicated a half-life of 77 days for the mixed activities. A battery of three off-gas scrubbers containing 1 M NaOH trapped about 0.01% of the total gamma activity associated with the stainless steel. Analyses of the scrubber solution indicated that essentially no free acid was carried by the hydrogen off-gas.

The exposed UO_2 pellets were dissolved in 125 ml of 8 M HNO_3 to produce a Purex-type feed solution containing uranium, plutonium, and fission products. About 50% of the iodine activity was volatilized and trapped in the off-gas scrubbers.

APPR Fuel Specimens. Uranium loss was excessive during the dissolution of pieces cut from a section of highly irradiated APPR fuel plate in boiling sulfuric acid (Table 6). These losses, which greatly exceed the 0.31% loss experienced with unirradiated specimens, suggest that exposure of the fuel core to the atmosphere by cutting pieces from the plate may have resulted in oxidation of the UO_2, such as believed to occur on the surface of irradiated UO_2 pellets exposed to atmosphere during long-term storage. Until dissolution tests can be conducted with an uncut APPR fuel plate or entire fuel assembly to establish whether or not excessive uranium loss occurs, the use of the Sulfex process for selective dissolution of stainless steel from APPR-type fuels must remain in doubt.

Table 6. Uranium Loss During Dissolution of Irradiated APPR Fuel Segments in Boiling Sulfuric Acid

Expt. No.	Fuel Wt (g)	Time (hr)	H_2SO_4 (M)	H_2SO_4 (ml)	Uranium Dissolved (mg/ml)	Uranium Dissolved (%)
1	7.5	2.5	6	600	0.30	94
2	15	3.5	6	500	0.40	41.7
3	15	4	4	750	0.38	39.3

Three unclad UO_2 pellets, ~20 g, which had been irradiated to 1000 Mwd/T and decayed 500 days, were exposed to boiling 4 and 6 M H_2SO_4 during three successive dissolutions of unirradiated 304L stainless steel coupons. Fairly low uranium and plutonium losses occurred during the second and third dissolutions; however, excessive losses occurred in the first experiment (Table 7). These results suggest that oxidation of the exposed surfaces of the UO_2 during storage may be responsible for the solubility of the uranium in the first experiment.

Unclad UO_2 Pellets Irradiated with Co^{60}. In order to determine whether continued radiation, possibly through the medium of hydrogen peroxide formation, affected the solubility of UO_2 in sulfuric acid decladding solutions, duplicate 60-g samples of sintered UO_2 pellets in 50 ml aliquots of 5 M H_2SO_4 were irradiated for 7 days in a Co-60 gamma source having a flux of 2.16×10^6 R/hr. Ambient temperature in the source was ~90°C. A third sample was refluxed at 90°C outside the source as a control.

By analysis, 4.9 mg of U per ml was found in the control, whereas the irradiated samples contained 5.2 and 7.4 mg of U per ml, an average increase of 30%. Whatever hydrogen peroxide formed during irradiation was not detected by subsequent analysis.

Table 7. Solubility of Uranium and Plutonium Oxides in Boiling Sulfuric Acid

Sintered UO_2 pellets: 20 g, irradiated to 1000 Mwd/T; decayed 500 days

Type 304L stainless steel coupons: 23 g, unirradiated

Reflux time: 4 hr

Expt. No.	H_2SO_4 (M)	H_2SO_4 (% Excess)	SS Diss. Rate ($mg/cm^2/min$)	Uranium (mg/ml)	Uranium (%)	Plutonium (counts/min/ml)	Plutonium (%)
1	4	125	1.22	1.30	2.9	2900	$\sim 10^{-3}$
2	4	275	>2.7	0.013	0.05	600	$\sim 10^{-4}$
3	6	275	>10	0.014	0.04	1700	$\sim 10^{-4}$

The results indicate that although the radiation effects slightly increased the solubility of the UO_2 in sulfuric acid, other mechanisms must be responsible for the high uranium losses experienced with APPR fuel where the UO_2 is finely divided and dispersed in the core.

4.0 WASTE TREATMENT

A brief investigation of evaporation as a means of reducing the volume of the spent sulfuric acid decladding solution prior to disposal as radioactive waste yielded discouraging results. A 25% volume reduction of decladding waste containing 5.6 M H_2SO_4 and 30 g of stainless steel per liter resulted in precipitation of ~60% of the iron at the boiling temperature. Another decladding solution containing 71 g stainless steel per liter and 4.7 M H_2SO_4 as free acid was neutralized with caustic; the neutralized solution occupied twice the volume of the unneutralized waste. Difficulty was experienced with evaporation because of bumping and solids formation. At 80% volume reduction, based on the original volume of unneutralized waste, a solid cake formed.[12]

The possibility of pit disposal of decladding-waste solution converted to a non-leachable solid led to experiments on neutralization with lime. The neutralization of 100 ml (from a dejacketting solution) of 5.5 M H_2SO_4 containing 22 g Fe, 5.3 g Cr, and 3 g Ni per liter with 0.55 mols of chemical lime produced a dry, solid cake of calcium sulfate incorporating the sulfate salts of iron, chromium, and nickel. The solidified cake occupied approximately the same volume as the unneutralized decladding waste. This cake was leached in 250 ml of distilled water for 60 days. At the end of this period, analyses of the slightly basic leach solution showed 0.42 g Ca per liter, 0.31 g SO_4 per liter, and less than 2 ppm of iron, chromium, and nickel.

A 160-ml sample of the same decladding solution was spiked with mixed fission products to a concentration of 1.0×10^7 gross beta counts/min/ml

and 6.4×10^6 gross gamma counts/min/ml. This solution was neutralized with lime, allowed to solidify, and leached with 900 ml of distilled water. After 10 days, radiochemical analysis showed that 1.7% of the gross beta and 5.7% of the gross gamma activities had been leached from the solidified waste; radio-cesium was the principal gamma activity. The cake was leached again with 3 liters of distilled water for 36 days; an additional 0.7% of the beta and 3.4% of the gamma activities were extracted from the waste. The iron, chromium, nickel content of the leach solution was less than 2 ppm, indicating that the stainless steel constituents were essentially fixed in the cake. Since the radioactivity of the decladding waste is principally due to activated components of stainless steel; solidification with lime may be quite useful as a pit disposal method.

Experiments on the neutralization of sulfuric acid decladding wastes with limestone chips, proposed for use in disposal pits, were unsuccessful because of "passivation" of the rock by a calcium sulfate surface layer.[12]

5.0 CORROSION STUDIES

Carpenter 20 stainless steel has been proposed as a potentially useful fabrication material for those pieces of process equipment which must contain sulfuric acid up to the boiling temperature. Table 8 summarizes the results of scouting-type corrosion experiments with unstabilized Carpenter 20. Weighed single specimens of tubing were fully immersed for 32 days in boiling 4 and 6 M H_2SO_4 solutions. Corrosion rates varied from 23 mpy (mils per year) in 4 M H_2SO_4 containing 24 g of stainless steel per liter to 62 mpy in pure 6 M H_2SO_4. Pitting and cracking occurred in all four experiments and specimen 4 was penetrated at a point which rested on a layer of precipitated salts of stainless steel.

Table 8. Corrosion of Carpenter 20 Stainless Steel in H_2SO_4

Specimens fully immersed 32 days at 100°C

Spec. No.	H_2SO_4 (M)	Stainless Steel (mg/ml) Initial	Final	Wt. Loss (g)	Area ($in.^2$)	Corrosion (mpy)
1	4	0	4.45	2.21	3.94	54
2	4	24	29	1.34	5.50	23
3	6	0	5.25	2.56	3.94	62
4	6	37	45	2.16	4.73	43

Unpublished data from Battelle Memorial Institute on the corrosion of niobium-stabilized Carpenter 20 in boiling pure 6 M H_2SO_4 showed rates, after 15 and 20 consecutive 3-hr exposures of 17.4 and 14.9 mpy, respectively. The rates in boiling 4 M H_2SO_4, after the same exposures, were 11.3 and 9.95 mpy, respectively. Battelle's results also indicated that the Carpenter 20Cb cracked badly when exposed to the acids in the absence of dissolved

stainless steel salts. Preliminary results suggest that the cracking is prevented by the presence of greater than 5 g of stainless steel per liter. Careful heat treatment also prevents cracking.

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APPENDIX I

YANKEE ATOMIC

	Core 1	Core 2
NUCLEAR		
Average Thermal Flux	~1 x 10^{13}	1.9 x 10^{13}
Thermal Power, Mw	392	480
Specific Power	18.3 kw/kg U	19.8 kw/kg U
Loading, kg U	21,400	24,200
Irradiation Time (full power days)	417	417
Load Factor, %	80	80
Burnup, Mwd/mg U	7,600	8,200
Enrichment Initially	2.6%	2.6%
Pu Produced	~5000 g/T U	~5000 g/T U
ELEMENT		
Type	Rod	Rod
Fuel	UO_2 Pellets	UO_2 Pellets
Pellet Diameter	0.30 in.	0.30 in.
Pellet Length	0.30 in.	0.30 in.
Pellet Density	10.2 g/cc	10.2 g/cc
Rod Active Length	90 in.	102 in.
Rod Total Length	~92 in.	104 in.
U Content, kg	0.92	1.045
Tube Material	304 SS	304 SS
Tube ID	0.305 in.	0.305 in.
Tube Thickness	0.015 in.	0.015 in.
Tube OD	0.336 in.	0.335 in.
Pellet Radial Clearance	0.0017 in.	0.0025 in.

SUB-ASSEMBLY	Cores 1 and 2
Type	Bundle
Number of Elements	64, 72, 80, or 81
Construction	The 8 or 9 rods of each row welded to notched strips which mesh with spacer strips to form roughly square bundle.
Rod Spacing	0.425 in. center-to-center on square pitch
Bundle Size	3.8 in. x 3.8 in. or 3.8 in. x 3.4 in. or 3.4 x 3.4 in.

ASSEMBLY	Core 1	Core 2
Type	Square Array	Square Array
Number of Rods	305 or 306	305 or 306
Number of Sub-assemblies	4	4
Construction	Bolted	Bolted
Over-all Length	107 in.	119 in.
Assemblies per Core	76	76
Outside Width	7.5 in.	7.495 in.
Active Section Before Irrad., kg		
UO_2	319	362
304 SS Clad	54	~60
304 SS Spacers	0.3	0.4
Active Section After Irrad., kg		
U^{235}	5.3	6.18
U^{236}	0.2	0.3
U^{238}	273	308
U	278	315
Pu^{239}	1.24	1.33
Pu^{240}	0.13	0.136
Pu^{241}	--	0.136
Pu	1.37	1.6
SS	54	~60
FP	2	2.6
O_2	38	43
Total Active Section	373	423
SS Rods, Ends	~45	~45
TOTAL ASSEMBLY	~418	~468

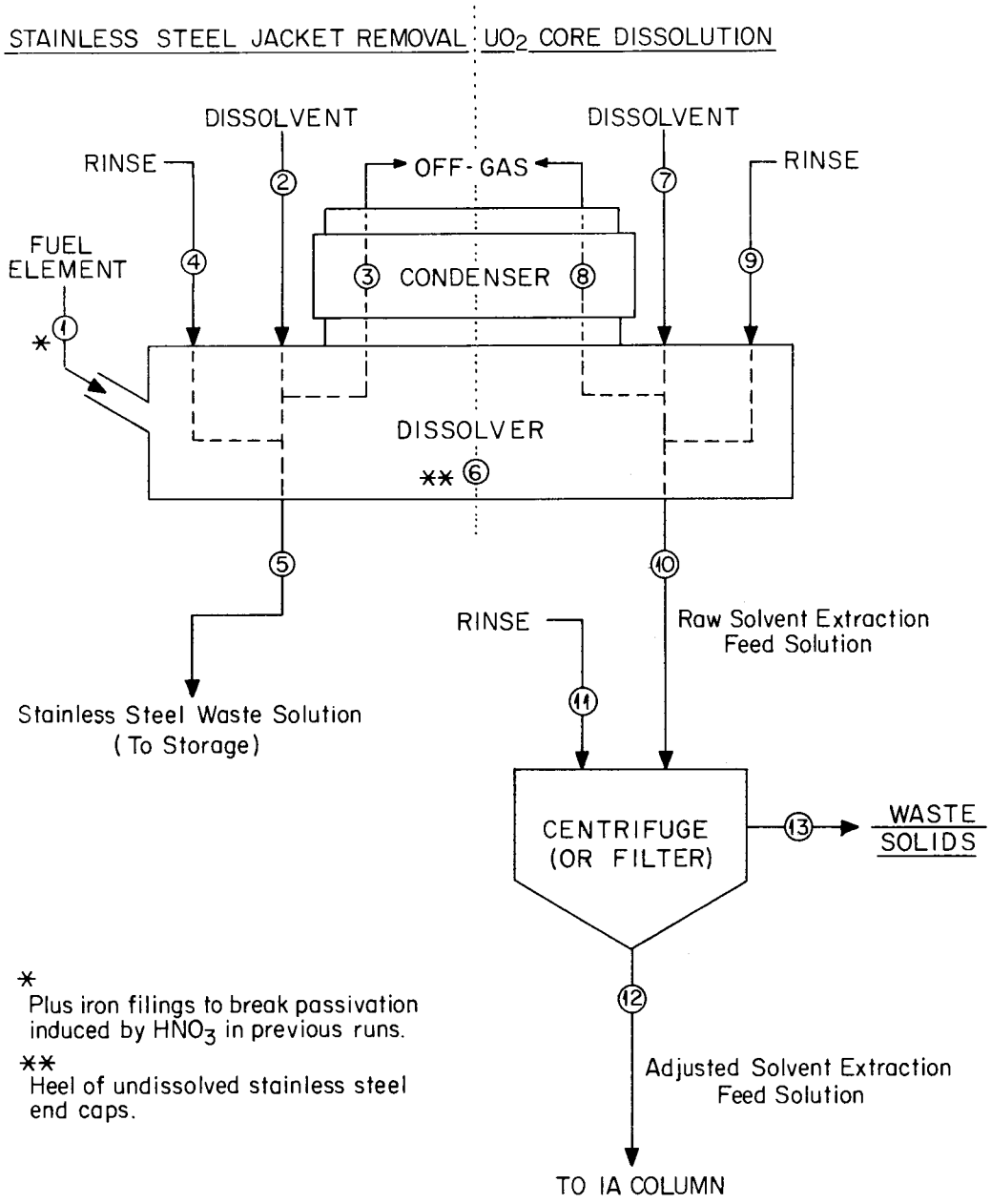
SHIPPING		
Cooling Time Before Shipment	90 days	90 days
*Uranium Shipped Per Year, kg	~15,000	~22,000
First Shipment	Oct. 1961	----

*Varies

(Henry C. Miksztowicz, Yankee Atomic Electric Co.,
441 Stuart Street, Boston, Massachusetts, CO-6-5800)

APPENDIX II

(Figures 7 and 8)



REACTION:

UNCLASSIFIED
ORNL-LR-DWG 27230-A

1. $Fe^{\circ} + H_2SO_4 \longrightarrow FeSO_4 + H_2$
   ΔH = 38.11 K-cal/mole Fe° Dissolved
2. $Ni + H_2SO_4 \longrightarrow NiSO_4 + H_2$
   ΔH = 33.21 K-cal/mole Ni° Dissolved
3. $Mn^{\circ} + H_2SO_4 \longrightarrow MnSO_4 + H_2$
   ΔH = 67.17 K-cal/mole Mn° Dissolved
4. $2Cr^{\circ} + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3H_2$
   ΔH = 57.46 k-cal/mole Cr° Dissolved
5. $UO_2 + H_2SO_4 \longrightarrow$ No Reaction
6. $2UO_2 + 6HNO_3 \longrightarrow 2UO_2(NO_3)_2 + NO + NO_2 + 3H_2O$
   ΔH = 30,955.2 K-cal/Assembly Core Dissolved

(Note: ΔH Values Calculated from Data Given in "Handbook of Chemistry and Physics.")

PROCEDURE:

1. Charge Fuel Element Into Dissolver.
2. Add ~400 gm Iron Filings to Prevent Passivation.
3. Add 4 M H_2SO_4 to Dissolver at 90°-100°C.
4. Digest at Reflux Temperature (~107°C) for 2 Hours.
5. Drain Dissolver and *** Rinse with 50 liters H_2O; Discard Dejacketing Solution + Rinse Water.
6. Add 727.65 liter of 8 M HNO_3.
7. Digest at ~100°C for 5 Hours.
8. Drain Dissolver Tank, Running Core Solution Through a Centrifuge (or Filter); Rinse Tank with 100 liters H_2O Which is Also Run Through the Centrifuge (or Filter).
9. Finally, Wosh Centrifuge (or Filter) with 72.35 liters H_2O and Add This Wash Solution to Core Dissolver Solution to Make Final Adjustment to Solvent Extraction Feed Conditions.

***The 50 liter Rinse Volume is an Arbitrory Number and May Vary Considerably Depending Upon Dissolver Design.

Fig. 7. Sulfex Process Flowsheet for Yankee Atomic Fuel.

Fig. 8. **Sulfex Process Chemical Flowsheet for Yankee Atomic Power Reactor Fuel**

Basis: one assembly with steel tie-rods mechanically removed

Stream No.	Volume (liters)	Mass (kg)	Sp. Gr. (g/cc)	U[a]		Fe		Cr		Ni		Mn		Si, kg	P, kg	C, kg	S, kg	H^+		SO_4^{--}		NO_3^-		H_2O		H_2		NO		NO_2	
				N	kg	*N*	kg	*N*	kg	*N*	kg	*N*	kg					*N*	kg	*N*	kg	*N*	kg	*M*	kg	*M*	kg	*M*	kg	*M*	kg
Streams In																															
1		431.0			319		47.6		12.4		5.52		1.38	1.38	0.69	Neg	Neg														
2	1,000.6	1,233.7	1.233															8.0	8.07	8.0	384.5			46,702	841.1						
4	50.0	50.0	1.000																					2,776.2	50.0						
7	727.6	908.8	1.249															8.0	5.87			8.0	361.0	30,093.8	542.0						
9	100.0	100.0	1.000																					5,552.4	100.0						
11	72.4	72.4	1.000																					4,017.2	72.4						
		2,795.9			319		47.6		12.4		5.52		1.38	1.38	0.69				13.94		384.5		361.0	89,141.6	1,605.5						
Internal Streams																															
6		5.4					3.74		0.98		0.43		0.11	0.11	0.05	Neg	Neg														
10	827.6	1,008.8	1.231	3.2	319									1.27		Neg	Neg	2.2	1.82			5.4	277.9	35,603	641.2						
Streams Out																															
3	28,343.8 (STP)	3.2																						39.6	0.71	1,225.8	2.47				
5	1,050.6	1,342.8	1.278	$\ll 0.001$[b]	<0.032	1.50	43.9[c]	0.63	11.4	0.17	5.09	0.044	1.27		0.64	Neg	Neg	5.3	5.60	7.6	384.5			49,438.6	890.4						
8	30,993.8	51.7																						43.2	0.78			670.2	20.1	670.2	30.8
12[d]	900.0	1,391.5	1.547	3.0	319											Neg	Neg	2.0	1.82			5.0	277.9	41,630.8	749.8						
13		1.3												1.27		Neg	Neg														
6		5.4					3.74		0.98		0.43		0.11	0.11	0.05	Neg	Neg														
		2,795.9			319		47.6		12.4		5.52		1.38	1.38	0.69	Neg	Neg		7.42		384.5		277.9	91,152.2	1,641.6	1,225.8	2.47	670.2	20.1	670.2	30.8

[a] As UO_2 or UO_2^{++} (the oxygen, ~43 kg, is not considered in U column, but is included in total mass column).

[b] U concentration $< 1.3 \times 10^{-4}$ or $\simeq$0.01% loss.

[c] As Fe^{++}

[d] Assume stainless steel dissolution rate of 3.5 mg·cm^{-2}·min^{-1} in 4 *M* H_2SO_4. The 0.015-in.-thick cladding dissolves completely in 1.5 hr (use 2 hr for safety factor). The end caps (1 in. long by 0.335 in. dia) do not dissolve completely, thus leaving a heel in the tank which can be removed after each dissolution or allowed to build up to a constant value of ~17 kg after 10 runs. Steel shot added at start of each new run breaks passivation induced by HNO_3.

APPENDIX III

(Reference ORNL-2225)

	APPR-1
NUCLEAR	
Average Thermal Flux	2.7×10^{13}
Specific Power	~ 0.5 Mw/kg U^{235}
Loading	22.5 kg U^{235} (including control)
Burnup	29% U^{235}
Life (80% Load Factor)	1.9 years

ELEMENT	Stationary	Control[a]
Type	Plate	Plate
Core Dimensions	0.020 x 2.50 x 22 in.	0.020 x 2.36 x 22 in.
Dimensions Including Clad[b]	0.030 x 2.78 x 23 in	0.030 x 2.56 x 23 in.
Core Composition, %		
UO_2	26	26
B_4C	0.14	0.14
SS Type 302B (2.4% Si)	Balance	Balance
Uranium Enrichment	93%	93%
Stainless Steel Clad	Type 304L	Type 304L

ASSEMBLY		
Type	Box	Box
Number of Elements	18(16 short, 2 long)	16(14 short, 2 long)
Plate Spacing	0.133 in.	0.133 in.
Side Plates	2	2
Side Plate Thickness	0.05 in. (SS)	0.05 in. (SS)
Side Plate Length	27 in.	24-13/16 in.
Construction	Brazed	Brazed

---

[a] Control assembly has Co-bearing flux suppressor combs on one end of fuel section and B^{10}-bearing absorber section at other end.

[b] Dimensions given for short plates. Stationary long plates have extra 2 in. of SS at each end; control long plates have extra 1-3/8 in. SS total both ends.

ASSEMBLY, continued	Stationary	Control
Cross-Section	2.863 x 2.838 in.	2.619 x 2.613 in.
Active Length	22 in.	22 in.
Over-all Length[a]	33-5/8 in.	26-1/8 in. (without absorber section)
Number Per Core	38	7
Composition Before Irradiation, g		
UO_2	632	512
U-235	515	418
B_4C	3.4	2.7
Haynes-25	--	180
SS in Core	1796	1465
SS in Clad	2010	1725
SS in Side Plates	900	1000[c]
Braze (10% Si)	40	35
Total Without End Adaptors	5381	4920
SS End Adaptors	2465	---
Composition[b] After Irradiation, %		
UO_2	8.9	8.0
Fission Products	2.9	2.0
Stainless Steel	88.2	92.0[d]
U^{235} After Irradiation		
Grams	366	297
Enrichment (%)	86	86

SHIPPING	
Cooling at Reactor	120 days
Discharge Rate	~15 kg U^{235} every two years
Casks per Core Shipped	5
First Shipment	August 1959

[a] Including adaptors (and handle on control).

[b] Without ends, but including handle and combs on control.

[c] Includes 160 grams for handle.

[d] Includes Haynes-25.

ORNL-2461

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