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CHEMISTRY — SEPARATION PROCESSES FOR PLUTONIUM AND URANIUM

UNITED STATES ATOMIC ENERGY COMMISSION

AN ANALYSIS OF POWER REACTOR FUEL
REPROCESSING

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March 27, 1957

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CHEMICAL TECHNOLOGY DIVISION

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Date Issued:

March 27, 1957

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0.0 ABSTRACT

This report presents an analysis of the projected economics and processing capacity requirements for a power reactor fuel reprocessing industry based on the recovery of fertile and fissionable materials from presently proposed power reactors within the confines of the continental United States for the next five to ten years.

An analysis of the present general state of development of a technology required for such an industry is given. A summary of results of power reactor reprocessing chemical and engineering development at Oak Ridge National Laboratory from July 1955 through December 1956 is given.

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PART I

ANALYSIS OF POWER REACTOR FUEL REPROCESSING REQUIREMENTS

To define a program for power reactor development, we have analyzed many facets of the nuclear fuel recycle in the past, particularly radiochemical reprocessing. In addition to this important step, we are attempting to define costs for phases of the reactor fuel recycle which follow radiochemical separation. From studies made during the past 18 months, we have drawn conclusions concerning the general questions posed in this part of this report; these conclusions have served as guides for drawing up the present program, which is discussed in Part II of this report.

1.0 ESTIMATE OF ALLOWABLE RECYCLE COSTS*

To specify the portion of the selling price of power in the United States that should be assigned to chemical processing is very difficult. We have assumed for some time (along with most other people working in the reprocessing field and those who have analyzed reactor costs) that the cost of radiochemical separations should not exceed 1 mill per kilowatt-hour of electricity, including profit, insurance, and taxes. Since there was no analytically derived reason for this assumption, we have made a try at defining allowable recycle costs.

J. W. Ullmann¹ recently attempted to define how much of the 8 mill/kwh selling price of electricity remains after reactor and fuel costs have been deducted. The results are shown in Fig. 1.1, which is a plot of allowable recycle costs vs. burnup for various reactor capital investment costs, assuming that electricity is to sell at 8 mills/kwh. From this cursory study of a thermal reactor, using 3% enriched fuel, it is unwise to draw conclusions that make use of the exact numbers developed. However, for the purpose of general guidance, we can observe that radiochemical reprocessing costs, which are only a part of the recycle cost, most assuredly cannot exceed 1 mill/kwh. This is supported by Fig. 1.1, which shows that for reactors requiring a capital investment of \$250/kw installed electrical capacity and operating to 4000 Mwd/t burnup, the total recycle cost cannot exceed \$17 per kilogram of uranium to achieve 8-mill/kwh power; this corresponds to 0.7-mill/kwh electricity. It is also important to observe that higher burnup does not increase the allowable recycle cost for this case.

Having established the fact that recycle cost should be less than 1 mill/kwh and that the probable radiochemical reprocessing cost must be less than half of this, we attempted to define the major parameters affecting chemical reprocessing costs.

We concluded that the reprocessing plant cost may be relatively insensitive to the type of chemical process, and that the important variables in unit cost may be chemical plant capacity and fuel burnup.

* Including radiochemical separations, waste disposal, metal reduction, fuel element fabrication.

BASIS:

AEC PRICE SCHEDULE OF 1/5/55
 INITIAL U^{238} RESONANCE ESCAPE
 PROBABILITY = 0.8
 20 MW HEAT/METRIC TON U
 3% U^{235} CHARGED
 80% LOAD FACTOR
 25% NET THERMAL EFFICIENCY
 145 MILLS/KWH OPERATION COST
 14 % ANNUAL CAPITAL WRITEOFF

Fig. 1.1. Relation of Investment, Irradiation Level and Processing and Fabrication Cost for 8 mill/kwh Power.

2.0 GENERAL STUDY OF COSTS VS. PLANT SIZE AND FUEL BURNUP

The next step in trying to develop a generalized understanding of the process economics was to estimate the probable cost of radiochemical reprocessing as a function of fuel burnup and chemical plant size. Because of the difficulty of analyzing the processing requirements for each type of power reactor fuel individually as a function of chemical plant size and because of the probable fallacy in the assumption that there will be only one or two types of reactor fuel in a mature power economy in the United States, we generalized the basis of our study by the following assumptions:

1. Chemical plants, and for that matter all the recycle plants, are capacity-sensitive to the total quantity of metal introduced as feed, not just the fissionable material content.
2. Most power reactors proposed to date are two-region (with enriched core and depleted or natural blanket), or single-region with partial enrichment. The average enrichment in these reactors is 1.5-2%, or about the same as that of natural uranium from the processing viewpoint.

We therefore have used metric tons of natural uranium as the nominal capacity unit and megawatt-days per ton of natural uranium as the burnup designation in our generalized studies.

Ullmann made a study of costs vs. the size of the nuclear economy and/or the radiochemical plant size.⁹ We have extracted three figures from this report which summarize the results. Figure 2.1 defines roughly the variation of plant capital investment as a function of plant size as determined in two studies.^{6,9} Figure 2.2 shows the variation of chemical reprocessing costs vs. the size of the nuclear power economy (assuming one processing plant) for various fuel irradiation levels. Figure 2.3 gives an estimate of the variation of cost parameter with chemical plant size. From these we have drawn the following conclusions:

1. To achieve chemical processing costs (products as nitrate solutions) of less than 0.5 mill/kwh of electricity, the chemical plant would necessarily have to process the fuel from 6,000-10,000 Mw of installed reactor electrical generating capacity, or as much as 40,000 Mw of heat at 25% thermal efficiency. At 4000 Mwd/t, the chemical plant would therefore have to process the equivalent of 10 tons of natural uranium per day. Making allowances for variation in thermal efficiency and the rather obvious limitations on the accuracy of the study, we concluded that a chemical plant of less than 5 tons/day capacity at an average burnup of 4000 Mwd/t could not yield processing costs of less than 0.5 mill/kwh. A 6- to 10-ton/day radiochemical plant would process the fuel output of 24,000-40,000 Mw of reactor heat generating capacity (6,000-10,000 Mw electricity), or 48 to 80 125-Mw (electrical) reactors.
2. Amortization of capital and other fixed charges make up most of the cost of operation. Therefore, a radiochemical plant should operate with a high on-stream factor.
3. Because of the diversity of the types of fuel being developed in this country for both stationary and mobile power reactors, we concluded that a

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ORNL-LR-DWG 9412A

Fig. 2.1. Capital Investment as a Function of Plant Capacity.

7

ORNL-LR-DWG16235

BASIS:
6²/₃ YEAR AMORTIZATION

-7-

Fig. 2.2. Recovery Cost as a Function of Irradiation Level and Size of Nuclear Power Economy.

Fig. 2.3. Cost Breakdown as a Function of Plant Size. Basis: 6 2/3-year Amortization, 2000 Mwd/ton.

large radiochemical plant should be a multipurpose facility, one in which it would be possible to process fuel from a different type of reactor within an economic shipping radius of the chemical plant.

To check this general conclusion, i.e., that a large plant could reduce costs to below 0.5 mill/kwh, we designed a large multipurpose plant (fuel from 32,000 Mw of reactor heat capacity) for proposed reactor fuels, using extrapolations of known and proposed technology.¹⁰ This required a capital investment and had operating costs as shown in Table 2.1. Unit costs of reprocessing fuel for various proposed reactors are shown in Table 2.2.

To support the concept of a central plant it was necessary to study the probable cost of shipping irradiated fuels from a power reactor site to a central chemical plant. The results (Table 2.2) of such a study¹¹ show shipping costs of less than 0.3 mill/kwh for distances as great as 1000 miles.

The economic picture that we have drawn indicates that, for production of 8-mill/kwh electricity, the following facts must hold:

1. The radiochemical processing cost must certainly be less than 1 mill/kwh and probably less than 0.5 mill/kwh.
2. The chemical plant must be capable of processing the output of many large power reactors, probably the irradiated fuel discharged from as much as 40,000 Mw of installed reactor heat capacity, assuming 4000 Mwd/t burnup.
3. Because of the variety of reactors being studied, the chemical plant should be capable of processing several, and probably many, different types of fuel.
4. The chemical plant must operate with a high on-stream efficiency because of high standby costs.
5. Costs incurred in shipping fuel from the reactor sites will not be excessive (for most reactors probably less than 0.3 mill/kwh) for distances up to 1000 miles.
6. High fuel burnup, even though burnup has a profound effect on over-all costs, will not change the requirement of a large central chemical plant. We are reasonably certain that a chemical plant with each reactor is not economically feasible.
7. The investment in a profit-earning radiochemical processing plant will be relatively large, probably of the order of \$75,000,000 to \$100,000,000.

We have now supported the general hypothesis that a large chemical plant could provide over-all fuel processing costs for most reactor schemes of less than 1 mill/kwh, and that the costs of shipping by rail half way across the United States plus the processing costs may be in many cases about 0.5 mill/kwh.

Table 2.1 Estimated Capital Investment and Operating Cost
of Multipurpose Radiochemical Processing Plant

	Investment	Annual Operating Cost (Including 15% Amortization)
Fuel storage and mechanical handling	\$14,944,000	\$ 6,912,000
Solvent extraction	33,380,000	14,463,000
Volatility	15,600,000	11,184,000*
Fission-product concentration	3,480,000	1,668,000
Waste disposal	6,490,000	Included above
Site development	11,140,000	
Services	9,100,000	
Total	\$94,134,000	\$34,227,000

*Volatility portion amortized in 2.4 years.

3.0 PREDICTIONS CONCERNING AVAILABILITY OF IRRADIATED FUEL TO SUPPORT A RADIOCHEMICAL REPROCESSING ECONOMY

Having reached this stage in our thinking, let us now look at the availability of irradiated fuel based on the various predictions of those interested in nuclear power growth. Fuel availability is a most significant consideration in determining when private industry can enter the recycle business for profit and whether chemical recycle development expenses can be financed by income from the sale of power at 8 mills/kwh or less. Our first estimates of the availability of fuel were based on the predictions of Lane, Knowlton, and the Atomic Industrial Forum, which are given in Fig. 3.1 for stationary power.¹² Assuming that our previous arguments are reasonably valid and that the growth of a nuclear power economy will not proceed faster than predicted by Lane, the earliest date that one large multipurpose chemical plant could be expected to make money with radiochemical processing costs of the order of 0.5 mill/kwh will be around 1967.

It is important that our generalized prediction be checked by actual growth and fuel supply potential. For over a year we have been tabulating reactor proposal data (obtained by following AEC announcements, classified data, newspapers, and technical journals, by direct letter and telephone contact, and from the CAP visitors to ORNL). A copy of our most recent compilation of this information is attached as Appendix I.

From an analysis of this information we have prepared the schedules and capacity estimates for U. S. stationary civilian power reactors shown in Table 3.1. It will be noted that this tabulation indicates that only 3920 Mw of installed heat capacity will exist by 1962, versus 6000 Mw predicted by Lane and 2000 Mw predicted by the AIF minimum. The 3920 Mw heat generating capacity is at least an order of magnitude too small to support one profit-making chemical plant.

The total irradiated fuel to be produced by 1962 from stationary civilian power reactors would comprise sufficient irradiated fuel to provide feed for a chemical plant of only 1.0 ton of natural uranium equivalent per day if burnups average 4000 Mwd/t. Both yearly production of irradiated fuel and the cumulative quantity, assuming no reprocessing, are shown in Table 3.2 for 1957-1962.

Fig. 3.1. Predicted Stationary Nuclear Power Growth. Basis: 25% efficiency in conversion of heat to electricity.

Table 3.1 Prediction of Available Irradiated Fuel From Stationary Power Reactors

Startup Date	Reactor	Heat (MW)	Region	Cladding Material	Bonding Agent	Fuel Composition and Chemical Form	Yearly Production of Irradiated Fuel			Th (kg)
							> 30% U ²³⁵ (kg of U ²³⁵)	3-30% U ²³⁵ (kg of U ²³⁵)	< 3% U ²³⁵ (kg of U)	
1957	HRT	5		--	--	UO ₂ SO ₄ (90% U ²³⁵ or more)	4			
	LAPRE-1	2		--	--	UO ₂ ** in 4M H ₃ PO ₄ (90% U ²³⁵ or more)	2			
	LAPRE-2	1		--	--	UO ₂ ** in 17M H ₃ PO ₄ (90% of U ²³⁵ or more)	1			
1958	BORAX 4	15		Al, Ni	?	UO ₂ , ThO ₂	20			
	EBWR	20		Zircaloy-2	Metal to metal	93.5% U, 1.5% Nb, 5.0% Zr (1.4% U ²³⁵)				2,000
	PWR	264	Seed	Zircaloy-2	Metal to metal	6% U, 94% Zr (90% U ²³⁵ or more)	130			
			Blanket	Zircaloy-2	None	UO ₂ (natural U)				15,000
	SRL	20		304 stainless steel	NaK	2% Zr, 98% U (2.8 U ²³⁵)				2,000
	Alternate			(304 stainless steel)	(NaK)	4.1% U, (90% U ²³⁵ or more), 95.9 Th	?			
	Pacific Gas & Elec. #1	12		Stainless steel	None	1.9% UO ₂ , (90% U ²³⁵ or more), 98.1% stainless steel	20			
	#2			Zr		UO ₂ (2.3% U ²³⁵)				?
1959	TBR-2	62	Core	Stainless steel	Na	98.4% U, 1.6% Zr (90% U ²³⁵ or more)	60			
			Blanket	Stainless steel	Na	U (depleted)				1,000
	CMBR	16		Stainless steel	None	UO ₂ , stainless steel (90% U ²³⁵ or more)	10			
1960	TBR	65	Core	--	--	UO ₂ SO ₄ (90% U ²³⁵ or more)	?			
			Blanket	--	--	ThO ₂ , D ₂ O				3,000
	APCA	300	Core	Zr	None or Na	10% Mo, 90% U (~25% U ²³⁵)		1,500		
	Alternate core		Core	(Zr)	(Na)	(2% Zr - 98% U) (~25% U ²³⁵)				
			End Blanket	304 stainless steel	Na	U (natural or depleted)				35,000
			Axial Blanket	304 stainless steel	Na	U (natural or depleted)				
	Cons. Pub. Power	240		304 stainless steel	NaK	U (2.27% U ²³⁵)				25,000
	Univ. of Florida	10		Stainless steel	None	UO ₂ , stainless steel (90% U ²³⁵ or more)	10			
Molverine	24		--	--	UO ₂ SO ₄ , D ₂ O	2				
1961	Piqua	45		Al	Ni	U (1.71% U ²³⁵)				3,000
	Comm. Ed.	620		Zircaloy-2	O	UO ₂ (1.48% U ²³⁵)				15,000
	Alternate			(Zircaloy-2)	(Metal to metal)	(High U, Low Zr, Av. 1.31% U ²³⁵)				
	Cons. Ed.	500	Core	Zircaloy-2	Metal to metal	9% U, 91% Zircaloy-2 (90% U ²³⁵ or more)	100			
			Blanket	Zircaloy-2	Metal to metal	Th				8,000
	Alternate			(Zircaloy-2)	(Metal to metal)	(4% U, 96% Th) (90% U ²³⁵ or more)				
	Rural Coop.	58	Seed	Zircaloy-2	Metal to metal	5.7% U, 93.4% Zr (90% U ²³⁵ or more)	8			
			Blanket	Zircaloy-2	Metal to metal	93.5% U, 1.5% Nb, 5% Zr (natural)				2,000
Yankee	480		304 stainless steel	None	UO ₂ (2.55% U ²³⁵)				20,000	
1962	Holyoke	44		316 stainless steel	None	77% UO ₂ , (10% U ²³⁵), 30% stainless steel		60		
	Chugach	37		Stainless steel or Zr	None or Na	93% U, 7% Mo or 98% U, 2% Zr or 99% U, 1% Si (1.5% U ²³⁵)				6,000
	PAR	530	Core	--	--	Homogeneous	?	--	--	?
	Florida Power	500	Core and blanket	--	--	Liquid Metal	?	--	--	?

Table 3.2 Predicted Rate of Production and Cumulative
Total of Stationary Power Reactor Fuel
1957 - 1962*

Enrichment	1957	1958	1959	1960	1961	1962
Rate (kg/year)						
> 30% U ²³⁵	7	177	247	252	360	360
3-30% U ²³⁵				1,500	1,500	1,560
< 3% U ²³⁵		19,000	20,000	80,000	120,000	126,000
Th				3,000	11,000	11,000
Cumulative Total, Assuming No Processing (kg)						
> 30% U ²³⁵	7	184	431	683	1,043	1,403
3-30% U ²³⁵				1,500	3,000	4,560
< 3% U ²³⁵		19,000	39,000	119,000	239,000	365,000
Th				3,000	14,000	25,000

* Not included are:
SRE, fully enriched U²³⁵ alternate;
Pacific Gas and Electric, 2.3% U²³⁵ alternate;
TBR, fully enriched U²³⁵ core.
A 2-type fuel plate design is assumed for the Consolidated Edison.

In Section 2.0 one of the conclusions was that 24,000-30,000 Mw of installed nuclear heat generation capacity would be necessary for a profit-making radiochemical plant. We have shown in this section that the loads may be as follows:

Estimator	Heat (Mw)				
	Stationary Nuclear Power			Proposed Reactors,	Propulsion Reactors,
	1962	1965	1975	1962	1965
Lane	6,000	13,000	64,000	3,920	1,000
Knowlton	6,000	17,000	100,000		
AIF (min)	2,000	3,400	--		
(max)	10,000	70,000	--		
McKinney	1,200	3,600	80,000		
report	to 5,000	to 13,000	to 300,000		

We must conclude that the quantity of irradiated fuel that will be available during the next five to ten years from both stationary and mobile power plants will not be adequate to support a private chemical plant. In fact, the quantities of fuel that may become available may be best suited to supply feed for the process pilot plant development and demonstration that are required before any nuclear power program proceeds beyond an experimental stage.

4.0 TECHNICAL STATUS OF RADIOCHEMICAL PROCESS DEVELOPMENT APPLICABLE TO REACTOR FUELS OTHER THAN PRODUCTION

The status of our knowledge, as measured by plant or pilot plant operation at full activity level, can be summarized by saying that we know how to separate:

1. Uranium from plutonium, while simultaneously separating both from fission products.
2. Thorium from uranium, while simultaneously separating both from fission products.
3. Enriched uranium from aluminum diluent and fission products.

These separations have been done only under the following limited conditions:

1. All feeds have been thorium and natural uranium metal or uranium-aluminum alloy.
2. Alloying and cladding metals have been aluminum only.
3. All fuels have been nitric acid soluble.

7. All fuels have been canned slugs or MTR type plates.

8. Very little mechanical disassembly has been done (British groups have used mechanical decanning; EBR-1 pins have been custom disassembled; fuel has been custom sawed).

9. Solvent extraction has been used almost exclusively, with the exception of the bismuth phosphate process, plutonium recovery by ion exchange by the Canadians, and some successful use of the same technique by British and United States groups for second and later plutonium product decontamination cycles.

We have had pilot plant experience with nonirradiated fuel on a process tailored specifically for the zirconium-containing fuel, in which HF is used as the dissolving acid; this process technique may or may not be satisfactory because of corrosion, problems associated with waste, and over-all cost. There has been similar pilot plant experience for stainless steel-containing fuels by a process using sulfuric acid as the dissolving agent; again, the process may or may not be successful. From studying the economics of these processes applied

to power reactor fuels (assuming that the processes can be adapted), it is evident that more economical process technology is required. We have made estimates comparing the above processes with the Darex and Zircex processes being developed here (Sections 6.0 and 7.0 of this report). The unit costs of recovery indicate cost differentials of factors of 1.5 to 3:

	Zirconium-Clad UO_2		Stainless Steel-Clad UO_2	
	Zircex	HF	Darex	H_2SO_4
Plant capacity (kg/day)	1000	1000	1000	1000
Unit cost (\$/kg U)	10.0	28.6	11.0	16.7

The types of processes that may be required for the various kinds of fuel proposed for the existing power reactor program are summarized in Tables 4.1.

A conclusion from Table 4.1 is that a large development program is necessary to produce any useful technology; in fact, even to have basic chemical processes, without pilot plant data, that are applicable to power reactors will require major effort and funds.

From the foregoing we have concluded that a major increase in effort in chemical processing is required. We have no technology now applicable to power reactor fuel processing; we have only an indication from our past work as to which direction our development effort should take. It is also relatively certain that the economic return possible from radiochemical reprocessing operations during the next ten years will be insufficient to attract private development and research money in anywhere near the requisite amounts. To illustrate, if we assume that reactor operators cannot afford to pay more than 1 mill/kwh for reprocessing in spite of the actual costs estimated in Fig. 2.2 and that 3% of the gross income is used for process research and development, the funds for such activities are:

Year	Stationary Power Generated (kwh) (Lane data)	Gross Income at 1 mill/kwh	3% of Total Yearly Income for Development
1962	1×10^{10}	\$ 10,000,000	\$ 300,000
1965	2.1×10^{10}	21,000,000	630,000
1975	1.3×10^{11}	130,000,000	3,900,000

Knowing approximately what it costs to develop radiochemical processes, we think we can safely conclude that funds will be insufficient to develop the required recycle technology—insufficient by factors of at least 10 to 30.

From the analysis of information in this section we cannot see how the private chemical industry can sponsor the vast recycle development program technologically required for nuclear power, particularly before there is evident income to support it.

Table 4.1 Status of Reprocessing Methods for Various Reactor Fuel Types

Process	Aluminum			Zirconium			Stainless Steel			Homogeneous		
	Th and < 3% U ²³⁵ Banford	10-40% U ²³⁵ Geneva	~90% U ²³⁵ MTR	Th and < 3% U ²³⁵ Common- wealth	10-40% U ²³⁵ APDA	~90% U ²³⁵ STR	Th and < 3% U ²³⁵ Consumers	10-40% U ²³⁵ Holyoke	~90% U ²³⁵ SIR	UO ₂ CO ₄ HRT	ThO ₂ PAR	U, B ₁ LMFR
Aqueous with conventional refabrication												
Volatility with conventional refabrication												
Pyrometallurgy with remote refabrication												

Key:

Has been operated on a significant scale with 'irradiate material'.

Ready for operation on a significant scale with irradiated material.

Undergoing engineering-scale development.

Undergoing laboratory-scale development.

Development not begun.

PART II

STATUS OF OAK RIDGE NATIONAL LABORATORY
POWER REACTOR FUEL REPROCESSING PROGRAM

A general research and development program for the reprocessing of privately financed power reactor fuels was started at Oak Ridge National Laboratory in July 1955. In this part of the report we will summarize and evaluate work completed through December 1956.

5.0 GENERAL POWER REACTOR FUEL REPROCESSING PROGRAM

The ORNL Power Reactor Fuel Reprocessing Program was undertaken in order to develop fuel recovery processes for classes of similar fuels and ultimately to demonstrate these processes through the pilot plant stage on significant capacity and activity levels with irradiated reactor fuels. A classification of fuels based on reprocessing principles is shown in Table 5.1.

We have adopted this program philosophy for several reasons. The multiplicity of reactor types currently proposed precludes the possibility of developing a tailor-made process for each fuel because of time, money, and manpower limitations. However, the similarity of many of the fuels makes it probable that processes applicable to all fuels of a common general type may be developed. A program approach is required that will ensure the immediate development of processes which make use of existing solvent extraction reprocessing technology for the new fuels, as well as stimulate the conception and development of new and applicable techniques which may improve chemical feasibility or economics of reprocessing. We are convinced that the power reactor fuel process development program must culminate in pilot plant chemical flowsheet runs, followed by such demonstrations as are required to define the engineering and economic aspects of the processes. We feel that private industry will be most reluctant to undertake the reprocessing of fuels for which proven chemical data and pilot plant demonstration are not available.

The scope of the present ORNL program includes chemical and engineering development and ultimate pilot planting of both aqueous and nonaqueous processes for the recovery of the several classes of reactor fuels. Our development philosophy is to investigate in the laboratory a number of chemical and/or mechanical methods for handling each type of fuel. The results of this scouting work are evaluated both technically and economically to select those methods which appear attractive. These then continue through intensive laboratory and preliminary engineering development stages.

The scouting efforts carried on during the past 18 months are tabulated below and are divided into stainless steel fuel processes, zirconium fuel processes, general design studies, and engineering equipment development. The bibliography, Section 15.0, at the end of this report should be consulted for the references.

For stainless steel-clad fuels we have studied the following possible processes:

1. Darex (dilute aqua regia).^{14-33, 38-40, 42}
2. Carburization.^{10, 14, 37, 38, 41, 42}
3. Electrolytic dissolution.^{14, 38, 41, 42}
4. Catalyzed nitric acid dissolution.^{14, 38, 39, 42}
5. Sulfuric acid.^{39, 40}
6. Molten metal dissolution.^{14, 36, 38, 41, 42}

Table 5.1 Classification of Heterogeneous Fuels Based on Solvent Extraction Reprocessing Principles

Classification	Principles
1. Enriched ($\sim 90\%$ U^{235}) UO_2 -stainless steel	<ol style="list-style-type: none"> 1. Requires criticality control 2. No plutonium recovery 3. Not directly HNO_3 soluble 4. High inert content (> 90 wt % stainless steel)
2. Enriched ($\sim 90\%$ U^{235}) uranium-zirconium alloy	<ol style="list-style-type: none"> 1. Requires criticality control 2. No plutonium recovery 3. Not directly HNO_3 soluble 4. High inert content (> 90 wt % zirconium)
3. Enriched ($\sim 90\%$ U^{235}) UO_2 , UC_2 , or uranium-aluminum alloy, plutonium-aluminum alloy or plutonium	<ol style="list-style-type: none"> 1. Requires criticality control 2. No plutonium recovery (enriched uranium case) 3. Soluble in HNO_3 catalyzed by mercury or fluoride 4. High inert content ($\sim 96\%$ aluminum for uranium-aluminum alloy)
4. Enriched ($\sim 20\%$ U^{235}) uranium metal, UO_2 , or uranium alloyed with zirconium, niobium, molybdenum, silicon, etc.	<ol style="list-style-type: none"> 1. Requires criticality control 2. Requires plutonium recovery 3. Soluble in HNO_3 (except for zirconium alloys*) 4. Low inert content ($< 15\%$ zirconium, etc.)
5. Natural or slightly enriched (U^{235}) uranium metal, UO_2 , or uranium alloyed with zirconium, niobium, molybdenum, silicon, etc.	<ol style="list-style-type: none"> 1. Essentially no criticality control 2. Requires plutonium recovery 3. Soluble in HNO_3 (except for zirconium alloys*) 4. Low inert content ($< 15\%$ zirconium, etc.)
6. Thorium	<ol style="list-style-type: none"> 1. Essentially no criticality control 2. Requires U^{233} recovery 3. Soluble in HNO_3 catalyzed by fluoride 4. No inert content

*Zirconium- and niobium-uranium alloys are explosive in pure nitric acid.

7. Mechanical processing.^{10,16-18,21-33,40}
8. Acid dissolution of core alloys.^{14-20,39,40}

For zirconium clad and/or zirconium clad-zirconium alloy fuels we have tried the following:

1. Zircex (gas phase and fused-salt phase).^{14-33,38-40,42,47,48}
2. Volatility (fused-salt dissolution).^{14,38-40,10,47-54,69}
3. Oxidation.^{14,34,37-39,41,42}
4. Electrolytic dissolution.^{39,41,42}
5. Molten-metal dissolution.^{14,38,39,41,42}
6. Acid dissolution (conc. H_2SO_4 , HF, aqua regia).^{14,18,20,39,40}
7. Mechanical processing.^{10,16-18,21-33,40}
8. Hydriding. (no references)
9. Nitriding. (no references)
10. Carburizing. (no references)
11. Dissolution procedures along with ultrasonics. (no references)
12. Hermex.^{43,44}

In addition to experimental work, we have done studies of general significance to the power reactor recycle:

1. Fission product growth and decay in thermal reactors,⁵⁵⁻⁶¹ including individual chains produced for fluxes of 5×10^5 n/sec/cm².
2. Product specifications for thorium⁶²; some preliminary work on UF_4 specifications.⁶³
3. Economic studies of interest to power reactor recycles.⁶⁴⁻⁶⁸
4. Growth, decay, and significance of heavy elements in thorium, U^{233} , U^{235} , U^{238} chains for all proposed conditions of irradiation with thermal neutrons.^{70,72,73}
5. Relative hazards in chemical plants due to radiation; long term biological hazards in wastes.^{71,74}
6. Waste processing and disposal.^{74,75}

7. The Hope Project,⁷⁸ which has served as a partial base for our engineering development programs.

We have carried out and are constantly expanding our general engineering development in such efforts as:

1. Shield design.
2. Improved samplers.^{79,80}
3. Pulse pumping.
4. Provisions for decontamination.⁸¹⁻⁸⁴
5. Plant arrangement for maximum economy.
6. Control of radiation exposure to operating and maintenance personnel.^{85,86}
7. Underwater maintenance.⁷⁸
8. Magnetic filters.⁸⁷
9. Sealed centrifuges.^{88,89}
10. Continuous in-line instrumentation.⁹⁰
11. Short-residence-time solvent contactor (jet-clone).⁹¹⁻⁹³
12. Cheap waste storage pits,^{21,94} as proposed in the Hope Project.⁷⁸
13. Criticality.^{5,78}
14. Continuous dissolution.⁹⁵⁻⁹⁷
15. Dissolver off-gas treatment,⁹⁸⁻¹⁰²

We feel that five major processes now under study are ready for intensive development, three for aqueous processing and two for nonaqueous processing.

The aqueous processing schemes are:

The Darex Process, applicable to all stainless steel-containing fuels, involves dissolution of the fuel in 5 M HNO₃-2 M HCl followed by distillation of the chloride to a concentration of 20 ppm or less, and solvent extraction of the residue.

The Zircex Process, applicable to all zirconium- and Zircaloy-2-containing fuels, involves reaction of the fuel with gaseous HCl or other inorganic chlorinating agents at about 350°C followed by distillation of chloride and solvent extraction of the residue.

A mechanical chopping plus selective leaching process is based on the fact that many stainless steel- and zirconium-clad fuels have nitric acid-soluble fuel alloys, oxides, etc.; therefore, we are actively engaged in developing means of exposing the active fuel material by various mechanical and chemical methods and then dissolving the active material directly in nitric acid. Solvent extraction would follow.

The two nonaqueous processes under development are:

The Fused Salt-Volatility Process, in which zirconium-containing fuels may be dissolved in molten fluoride salts in the presence of HF, followed by uranium fluorination to UF₆, which volatilizes from the fused salt and is then decontaminated and recovered.

The Hermex Process, a low-temperature zero-valence-state process in which uranium can be dissolved in boiling mercury, the resulting U-Hg intermetallic compound separated from the slag, cooled, washed with HCl, filtered, and retorted to remove the mercury and remelt the uranium.

Alternate subsidiary processes are discussed in detail in Section 9.0 of this report.

The application of existing and modified solvent extraction chemistry and engineering to the aqueous solutions obtained by the dissolution and feed preparation procedures will require considerable effort. Such effort will determine what flowsheet and equipment modifications must be made so that a common solvent extraction plant can be used for decontamination and fissionable-fertile material separation.

For purposes of review and reporting of the status of development, we have divided our program somewhat arbitrarily into the following major problems:

<u>Subprogram</u>	<u>Type of Effort</u>
Stainless steel process (Darex)	Chemical and engineering development
Zirconium process (Zircex)	Chemical and engineering development
Mechanical processing	Chemical and engineering development
Alternate aqueous processes	Chemical development
Solvent extraction	Chemical and engineering development
Hermex	Chemical and engineering development
Volatility applications- dissolution studies	Chemical and engineering development and pilot planting
Design engineering	Design and cost studies, design of pilot plant(s)

We do not propose to develop a process for each reactor fuel but believe, rather, that a general process technique should be developed for as many reactor fuels as possible. It is highly probable that any other approach, such as the assignment of individual fuels as specific development problems, will result in great duplication of effort and high development cost. Further, we are convinced that a multipurpose pilot plant, using common solvent extraction process equipment as a base, is a required and integral part of any development program.

The processes which we now indicate as being the most attractive may not prove feasible or operable as further development data are collected. For this reason we will continue to search for new techniques and to carry on certain of the process studies already started (see Section 9.0).

6.0 STAINLESS STEEL FUEL PROCESSING (DAREX)

W. E. Clark, M. L. Hyman, A. H. Kibbey,
F. G. Kitts, and J. J. Perona

6.1 Objective

We are endeavoring to develop a process for dissolution of all types of stainless steel-containing fuels in a single head-end set of equipment with a minimum of mechanical processing. Although chopping-leaching of stainless steel-clad fuels with nitric acid-soluble core material appears attractive, it is not applicable to UO_2 -sintered stainless steel mixtures. At present, the Darex process,^{14-33,38-40,42,45} in which the fuel is dissolved in dilute aqua regia and the HCl subsequently distilled off, appears to be the most promising process for stainless steel-containing fuel element processing. The uranium would be recovered from this solution by solvent extraction.

6.2 Status

Dissolution rates, distillation data, corrosion data,* and initial solvent extraction runs on a laboratory scale with nonirradiated fuel indicate that the process has a good chance of success. The outstanding problems that remain are demonstration of continuous equipment, both on a laboratory and engineering scale; demonstration on highly irradiated fuels; and evaluation of the corrosion and maintenance problem in engineering-scale equipment for a significant period of time.

6.3 Data

An idealized flowsheet is now being tested (Fig. 6.1). The fuels are dissolved in 5 M HNO_3 -2 M HCl, and the resulting solution is passed countercurrently to azeotropic (15.2 M) HNO_3 where the chloride is stripped from the liquid to less than 20 ppm. The overhead gases are recovered in a rectifier; any noncondensable chloride vapors are passed to a nonradioactive waste system via a caustic scrubber. Still bottoms, containing the metals in solution, pass to a feed-preparation step where any remaining chloride is removed by decomposition during the feed-boil-down step.

The advantages of this method include rapid dissolution of fuel of all configurations in a single head-end dissolver system, elimination of mechanical processing, hydrogen-free dissolver off-gas, and continuous high-throughput operation. The principal disadvantages are corrosion and the carrythrough of inert metals to the radioactive waste storage system.

The average dissolution rate of stainless steel is rapid and varies from 2.0 to 78 $\text{mg}/\text{cm}^2/\text{min}$ for batch dissolutions and 25 to 130 $\text{mg}/\text{cm}^2/\text{min}$ for continuous dissolution, depending on acid and metal concentrations (Figs. 6.2 and 6.3). These rates are very favorable when compared to the 3 to 5 $\text{mg}/\text{cm}^2/\text{min}$ normally considered to be satisfactory. Insoluble fines collected from the batch dissolution of a portion of an APFR plate were found by spectroscopic analysis to contain mostly

* Subcontract with Battelle Memorial Institute.

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Fig. 6.1. Darex Process.

Fig. 6.2. Dissolution Rate of Stainless Steel in HCl-HNO₃.

Fig. 6.3. Reaction Rates for the Dissolution of 304 Stainless Steel in Aqua Regia.

chromium and less than 0.1% uranium. Particle sizes ranged from about 2.5 to less than 0.1 μ . The concentration of stainless steel in the dissolver product solution varies with the acid feed rate; data for two acid feed compositions are given in Fig. 6.4. Dissolution is not the limiting processing rate for the Darex process, as is often the case with other type fuels, and less rapid dissolution conditions can be chosen to reduce corrosion and the heat production rate, or achieve other objectives. Experimental bench-scale continuous dissolvers are shown in Figs. 6.5 and 6.6.

Considerable decomposition of chloride to volatile chloride compounds occurs during the dissolution reaction, amounting to 22% in the case of a 15-min batch dissolution, to 46 g/liter, of type 304 stainless steel, using 5.0 M HNO_3 —2.0 M HCl . A maximum of 8% decomposition was observed at one stage of the stripping process when 15.2 N HNO_3 was used. The amount of chloride recovered in the rectifier during continuous operation is not known as yet.

Vapor-liquid equilibrium data for the $\text{HCl-HNO}_3\text{-H}_2\text{O}$ system are presented in Fig. 6.7. Data from batch and continuous stripping experiments on hydrochloric acid—nitric acid solutions containing 70–85 g/liter of dissolved APPR fuel element are presented in Fig. 6.8 and Fig. 6.9. These data demonstrate the feasibility of reducing the chloride to a value (approximately 7×10^{-3} M, or 20 ppm) suitable for use in existing stainless steel solvent-extraction equipment.

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Fig. 6.4. Product Stream Concentration for the Dissolution of 304 Stainless Steel in Aqua Regia.

Fig. 6.5. Laboratory Scale Continuous Darex Dissolving Equipment.

Fig. 6.6. Bench Scale Continuous Darex Dissolving Equipment.

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Fig. 6.8. Chloride Stripping by Nitric Acid Reflux.

Fig. 6.9. Chloride Concentration Profile for Darex Distillation.

7.0 ZIRCONIUM FUEL PROCESSING (ZIRCEX)

R. J. McNamee, J. J. Perona, and J. E. Savolainen

7.1 Objective

The most promising method developed thus far in our laboratory studies for zirconium- and Zircaloy-containing fuels is the Zircex process, in which the metallic zirconium and uranium are hydrochlorinated at around 400°C to form volatile $ZrCl_4$ and solid UCl_3 . Thus the zirconium is eliminated as a volatile product, while the UCl_3 remains as an ash. This process shows promise as a "universal" process on zirconium-containing fuel, but is, as yet, not developed beyond the laboratory scale. The UCl_3 product from the Zircex process might be processed further by the fused salt volatility process or by the Hermex process, as well as by aqueous nitrate solvent-extraction methods. Zircex should eliminate zirconium-uranium and niobium-uranium intermetallic compounds and consequently the hazard associated with their dissolution in nitric acid systems.

An exothermic hydrochlorination reaction between zirconium and HCl gas takes place at the sublimation temperature of the zirconium chloride, 331°C, or higher. The hydrochlorination may be carried out with a gas-phase reagent, hydrogen chloride, as indicated in the flowsheet in Fig. 7.1, or with a liquid-phase reagent, such as fused aluminum ammonium chloride, as shown in Fig. 7.2. An intensive effort will also be made to extend this technology to niobium-alloy fuels.

7.2 Status

The Zircex gas- and liquid-phase processes are in the early stages of development and their over-all potentialities are not known. They have the advantage of attacking all configurations of and proposed alloys of zirconium-containing fuels, and hence eliminate or minimize mechanical processing and aqueous dissolution of metal. They also eliminate zirconium from the solvent extraction or fluoride volatility feeds. Consequently, an increase in plant capacity and minimized radioactive waste storage volumes may be obtained.

The principal operational problems are (1) uranium losses either as volatile products or as insoluble compounds in the ash, (2) corrosion, and (3) dissipation of heat of reaction during hydrochlorination and fission product heat following the reaction. Uranium volatility losses are not excessive in laboratory-scale experiments, but final evaluation is needed in engineering-scale equipment. Uranium loss in the ash is not a problem in jacket removal or low-zirconium alloy applications, but requires considerable study in the cases where complete hydrochlorination of high-zirconium alloys is required. The fate of plutonium is not known at present. The use of cobalt-base alloys as a material of construction appears to be practical in the gas-phase system. A systematic search for a material of construction for the liquid-phase system has not been made as yet.

In regard to heat dissipation, the use of the gas-phase reaction appears to be limited to zirconium de-jacketing and low-zirconium alloys, where heat production both during and after reaction is relatively small. For highly enriched U^{235} fuels, where the amounts of zirconium and fission products are large and hydrochlorination of the entire fuel assembly is required, use of a liquid hydrochlorination agent is believed required to control the heat removal both during and after hydrochlorination.

Fig. 7.1. Zircex Process, Gas Phase Hydrochlorination.

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Fig. 7.2. Zircex Process, Liquid Phase Hydrochlorination.

7.3 Data

A great number of data already have been obtained on both the gas- and liquid-phase reactions.^{10,14-33,38-40,42} However, many of these data are of a preliminary nature and require considerable amplification and further engineering-scale effort prior to final verification of the Zircex process.

Gas-phase Reaction Rates In general, both uranium losses and rate of reaction of fuels with HCl gas increase with both temperature and alloy inert content (Table 7.1). The rates for uranium metal and oxide and high-uranium alloys are sufficiently low to permit use of the Zircex process for zirconium jacket removal. In engineering-scale tests on 300-g samples, the reaction rate increased from 2.5 to 27.0 mg/cm²/min as the temperature increased from 400 to 700°C and as the amount of uranium in the uranium-zirconium alloy increased from 0 to 60 wt % at a constant HCl partial pressure of approximately 0.6 atm. A plot of the logarithm of the reaction rate versus reciprocal temperature is roughly linear (Fig. 7.3). The reaction rate at a given temperature increases with increasing uranium content, but the effect of increasing uranium content on reaction rate becomes less as the temperature increases. For example, at 400°C the spread in the reaction rates for the various alloys is approximately a factor of 4, whereas at 700°C the spread is only a factor of 1.5.

In laboratory experiments 99% of the Zircaloy-2 cladding was removed from a typical (PWR blanket) uranium dioxide fuel element by hydrogen chloride gas at 600°C in 2.4 hr. Over 99.9% of the exposed UO₂ was then dissolved in nitric acid in about 1 hr. Enough HCl remained in the nitric acid solution to require a Darex distillation step following dissolution.

A picture of a zirconium-uranium alloy sample before and following incomplete hydrochlorination is shown in Fig. 7.4, and the insulated inconel engineering-scale hydrochlorinator in Fig. 7.6.

Gas-phase Reaction Uranium Losses In general, the uranium loss to the sublimate in laboratory experiments increased with temperature and was higher for alloys containing molybdenum or aluminum than for those containing zirconium or niobium (Table 7.1). In laboratory equipment the volatile uranium loss was excessive in the case of zirconium-uranium or niobium-uranium alloys at temperatures above 500°C; however, these losses are undoubtedly a function of equipment design and scale and should not be taken as exact parameters, since in a single run on an engineering scale with 60% uranium—40% zirconium alloy at 600°C, the uranium loss due to entrainment and vaporization was less than 0.02%.

The amount of uranium lost as residue insoluble in boiling 8 M HNO₃ increased with hydrochlorination temperature in the case of Zircaloy-2-containing fuel (STR) but showed no general pattern for other alloys (Table 7.1). The loss in the residue from the hydrochlorination of 60% uranium—40% zirconium alloy at 600°C decreased from 2.0% after 1 hr digestion in 8 M HNO₃ to 1.2% after 24 hr digestion. The loss to the residue in the case of zirconium-containing fuels appears to be a function of the amount of zirconium oxide initially present, which apparently forms a solid solution with uranium. Both cubic and monoclinic forms of ZrO₂ have been identified

Table 7.1 Effect of Temperature on the Gas-phase Zircex Process

Laboratory-scale reaction with anhydrous HCl gas
followed by dissolution of the ash in boiling 8 M HNO₃

Alloy	Temperature (°C)	Rate (mg/cm ² /min)	U Distribution (% of total)		
			In Hydrochlorinator		In Sublimate
			Soluble in boiling 8 M HNO ₃	Insoluble in boiling 8 M HNO ₃	
Zircaloy-2-clad U- Zr alloy	300	2.32	99.9	0.08	0.02
	330	3.13	96.3	1.35	0.05
	450	2.97	95.6	4.2	0.08
	600	4.20	55.5	7.73	36.8
	750	10.0	9.17	23.0	67.9
99.25% U-0.41% Zr- 0.12% Nb-0.22% Mo	400	0.13	97.6	2.2	0.2
	500	.42	98.3	1.2	0.5
	600	2.22	93.2	0.3	6.5
90% U-10% Mo	400	2.96	99.9	---	0.1
	500	10.3	99.4	---	0.6
	600	24.0	88.3	0.1	11.6
93.4% U-5.3% Zr- 1.3% Nb	400	7.65	99.9	<0.1	<0.01
	500	7.33	99.9	<0.1	<0.01
	600	2.78	99.8	<0.1	0.1
97.9% U-2.1% Zr	400	1.25	99.9	0.08	<0.01
	500	2.83	99.7	0.26	<0.01
	600	9.55	99.3	0.65	0.09
98% U-2% Nb	400	0.77	98.7	1.26	<0.01
	500	0.79	99.5	0.48	0.04
	600	0.75	97.7	1.04	1.24
15% U-85% Al	400	2.14	69.6	1.24	29.2
	500	1.04	83.6	1.11	16.2
	600	3.93	27.6	0.4	72.0

Fig. 7.3 Hydrochlorination Rates in Engineering Scale Equipment for Zirconium-Uranium Alloys as a Function of Temperature.

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Fig. 7.4. Sample of U-Zr Alloy Before and After Partial Hydrochlorination.

Fig. 7.6. Photograph of Engineering Scale Hydrochlorination Unit.

in the insoluble ash. If these uranium losses prove to be excessive, they could be recovered by treating the residue with carbon tetrachloride at 350°C to form soluble chlorides or by dissolution in fluoride solutions.

Gas-phase Reaction Heat Dissipation. In the hydrochlorination reaction roughly 40% of the heat of reaction is removed by convection, 55% by radiation, and the remainder as sensible heat. Emissivity constants of zirconium-uranium alloys undergoing hydrochlorination have been calculated by energy balances and vary from 0.22 to 0.89. Typical constants are plotted against temperature for several fuel compositions in Fig. 7.7. The emissivity of Zircaloy-2 and 7.3% uranium-zirconium alloy increases with increasing temperature; however, for 20, 40, and 60% uranium-zirconium alloys the emissivity coefficient tends to increase with increasing uranium content but decreases with increasing temperature. Calculated natural convection coefficients for the various runs varied from $2.3 \text{ Btu/hr}\cdot\text{ft}^2\cdot^{\circ}\text{F}$ to $3.7 \text{ Btu/hr}\cdot\text{ft}^2\cdot^{\circ}\text{F}$.

Behavior of Fission Products and Plutonium in the Gas-phase Reaction. The retention of radioactive fission products by the uranium chloride intermediate product of the Zircex process as applied to zirconium-uranium alloy fuels is shown in Table 7.2. Most of the ruthenium, cesium, and rare earth activity remains in the uranium chloride residue, along with all the detectable strontium activity. The fission product distribution data were obtained with tracer level activities; this work will be repeated later at high activity levels. In addition, the behavior of plutonium in the concentrations expected at full levels of irradiation will be investigated.

Gas-phase Reaction Corrosion Data. Materials of construction for use in the Zircex process are being investigated under a subcontract with Battelle Memorial Institute. The main reaction vessel must withstand gaseous hydrogen chloride and hydrogen at elevated temperatures in the first step of the process, followed by a water wash to remove soluble chloride salts. Thin plates or pin type elements could be completely chlorinated, and hence the residual chloride ash would be quantitatively flushed out in this manner. However, uranium metal or oxide and high-uranium-alloy fuels would remain as solids which would require dissolution in 8 M HNO_3 . Cobalt-base alloys, such as S-816, appear to give satisfactory corrosion rates for both hydrochlorination and boiling nitric acid.

Liquid-phase Reaction Data. The liquid-phase Zircex process was devised to reduce or eliminate some of the engineering problems associated with the gas-phase process, particularly heat dissipation. The fuel element is dissolved in aluminum ammonium chloride (or other inorganic hydrochlorinating agent), which serves also as a heat control and exchange medium.

Zirconium, Zircaloy-2, thorium, and uranium all dissolve rapidly in molten aluminum ammonium chloride. Zircaloy-2 dissolves at a rate of $7.65 \text{ mg/cm}^2/\text{min}$ at $330\text{--}370^{\circ}\text{C}$, and thorium at a rate of $4.9 \text{ mg/cm}^2/\text{min}$. When zirconium is reacted at 400°C under refluxing conditions, the zirconium tetrachloride formed leaves the melt as a vapor. In this way about 95% of the zirconium is separated from the uranium fuel during the dissolution step. The uranium and thorium form chlorides which are nonvolatile and dissolve in the melt. Further studies have shown that the aluminum ammonium chloride can be distilled, leaving uranium and thorium chlorides as nonvolatile residues. About 0.2% of the uranium is volatilized with 67% of the melt.

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Fig. 7.7. Emissivity of Zirconium-Uranium Alloys vs Temperature.

Table 7.2 Distribution of Fission Products
in the Zircex Process

<u>Activity</u>	<u>Amount Retained in Uranium Residue (%)</u>
Gross β	52
Gross γ	24
Ru γ	98.7
Zr γ	1.8
Nb γ	5.0
Cs γ	95
TRE	99.8
Sr	> 99.999

8.0 MECHANICAL PROCESSING AND NITRIC ACID LEACHING G. A. West, F. G. Kitts, C. V. Chester

8.1 Objective

The prime objectives of the mechanical processing of reactor fuels prior to chemical operations are: (1) to eliminate as much inert material, such as end boxes, as possible and to separate core and blanket sections in a common fuel assembly; (2) to loosen and remove the cladding from nonmetallurgically bonded fuels with nitric acid-soluble core material such as uranium, UO_2 , thorium, U-Si, and U-Mo; and (3) to break down the cladding in metallurgically bonded fuels with nitric acid-soluble core materials so that the cores can be leached from the cladding with nitric acid and the clad subsequently discarded. Elimination of inert material prior to solvent extraction will increase throughput and decrease waste storage requirements in an operating plant. The elimination of chemical processing of cladding material by nitric acid leaching will permit the use of existing process technology, with only minor modifications, for all nitric acid-soluble core materials.

8.2 Status

At the present time work under the mechanical processing subprogram^{10,16-18, 21-33,40} includes (1) the testing and evaluation of a variety of standard equipment prototypes which may be used in fuel handling and (2) design, cost, and feasibility studies on special equipment and equipment sequence and arrangements. The general mechanical processing plan for handling fuel from receipt to chemical dissolution is indicated in the schematic flowsheet in Fig. 8.1. Equipment currently on hand is being used to demonstrate fuel chopping, electric spark cutting, roll expansion, and sawing of fuels. Feasibility design studies are in progress here; a subcontract with American Machine and Foundry Atomics, Inc., currently is being implemented to obtain conceptual design of mechanical-handling equipment and to ascertain which mechanical applications have the greatest possibility of success.

8.3 Data

Equipment Evaluation. Results of tests with an Elox electric spark cutter (Figs. 8.2 and 8.3), a Mackintosh-Hemphill rotary straightener, and a conventional shear (Fig. 8.4) are summarized below.

The cutting methods studied include cutting with torches, electric arc cutting, milling, electrical discharge cutting, and conventional sawing. Only the last two appear to be usable in fuel processing. The Elox electric-spark-cutting technique has been successfully demonstrated on unirradiated stainless steel Army Package Power Reactor fuel (Fig. 8.5). With a rotary sacrificial brass electrode, slit-like cuts were made simultaneously between each two of 18 plates at a rate of 15 linear in./hr. The Elox machine has a high probability of success when used with stainless steel-clad fuels. The effect of electrical-discharge underwater cutting on pyrophoric metals such as uranium, zirconium, and thorium is not now known. At this time, Elox cutting would be used only for operations which conventional sawing or cutting could not accomplish.

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Fig. 8.1. Mechanical Processing Flowsheet.

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PHOTO 19390

Fig. 8.2. Side View of Elox Electric Discharge Cutter.

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PHOTO 19389

Fig. 8.3. End View of Elox Electric Discharge Cutter.

Fig. 8.4. Conventional Power Shear.

Fig. 8.5. Elox Electric Discharge Cutting of APPR Assembly.

The decladding of stainless steel synthetic fuels and Oak Ridge National Laboratory slugs with a rotary straightener has been satisfactorily demonstrated. Stainless steel-clad drill rods (carbon steel), 0.60 in. dia and 36 in. long, containing water to simulate a Na-K bond (0.006 in. thick) between core and cladding, were declad in four or five passes through the Mackintosh-Hemphill machine. At least one stainless steel end cap was removed by the rolling operation. Similar rods wrapped with stainless steel wires 1/32-in. dia on a 12-in. pitch to simulate spacers in a fuel bundle were declad by expansion and splitting of the jacket. As the spacer was flattened during rolling, the cladding was indented under the wire. Additional rolling caused the cladding to split in the indented areas.

Oak Ridge National Laboratory slugs were declad rather easily after four or five passes through the straightener. 25 ORNL slugs were satisfactorily processed. Dimensional changes, averaged from measurements made on several slugs of each type, are given in Table 8.1. Declad fuel prototypes are shown in Fig. 8.6.

Coextruded zirconium-clad unirradiated natural uranium fuel rods approximately 3 ft long were easily declad by expansion and cracking of the zirconium cladding. It appears that a true metallurgical bond was not effected between the zirconium and uranium, although breaking such bonds has not been proved impractical.

Shearing of zirconium- and stainless steel-clad fuel rods (or single plates) appears very practical at this time, although shear blade life for uranium, UO_2 , and UO_2 -stainless steel sinters has not been established. Consultation with industrial experts on shearing reveals that fuel assemblies (bundles of rods or plates and laminates) cannot be sheared without rapid destruction of shear blade (die) sets.

Design Studies. Specific design studies are in progress for an underwater sawing facility and a continuous nitric acid leacher.

Conceptional designs of two underwater saws for dismantling fuel assemblies into subassemblies and subassembly components as required have been made for comparison and cost studies. In the first design (Fig. 8.8) an abrasion disk saw is capable of making transverse cuts only on fuel assemblies 8 in. dia by 13 ft long. The other design is capable of handling the same fuel assemblies but with an added feature permitting full-length longitudinal cuts. It appears likely from this paper study that both saws have a high probability of being used successfully in an actual installation.

Sheared pieces of zirconium or stainless steel-clad fuels containing readily soluble nitric acid cores should in many cases be dissolved on a continuous basis. A dissolver that can accept fuel pieces and discharge the insoluble clads continuously is required for such an operation. A critically safe rotary continuous dissolver with solids discharge has been designed (Fig. 8.9) and a demonstration model is being fabricated.

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Table 8.1 Dimensional Data on Roll-declad Fuel Slugs

	<u>Oak Ridge National Laboratory Slug</u>		
	<u>Original</u>	<u>After</u>	<u>Dimensional</u>
	<u>Dimension</u>	<u>Rolling</u>	<u>Change</u>
Length of tubular cladding (in.)	3.86	3.76	-0.10
O.d. of cladding (in.)	1.18	1.32	0.14
Wall thickness of cladding (in.)	0.042	0.038	-0.004

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Fig. 8.6. Fuel Slugs After Roll Decloadding.

Fig. 8.8. Isometric View of Underwater Saw Design No. 1.

Fig. 8.9. Critically Safe Rotary Slab Dissolver with Continuous Solids Feed and Discharge.

Mechanical Processing Subcontract. A subcontract is being let to AMF Atomics, Inc., to make a feasibility paper study, preliminary cost estimate, and conceptional machine designs for the various mechanical operations outlined here. This study is to be completed in approximately six months. Promising operations may be investigated to the extent of designing, constructing, and testing of prototype machines.

9.0 ALTERNATE HEAD-END PROCESSES FOR SOLVENT EXTRACTION

9.1 Objective

A number of head-end methods are being surveyed to determine relative technical and economic feasibility as compared to the Zircex, Darex, flowsheets. Each method will be developed to the point where enough data is available to permit a comprehensive economic evaluation.

9.2 Carburization of Stainless Steel Fuels (R. E. Adams, J. E. Savolainen)

Status. Carburization-dissolution studies in the Metallurgy^{76,77} and Chemical Technology Divisions^{10,14,37,38,41,42} show that uranium can be quantitatively leached from carburized stainless steel fuels by nitric acid. Considerable additional work is required to optimize conditions to ensure complete carburization and prevent passivation. The fate of plutonium is not known. Initial cost estimates indicate that carburization is less desirable than the Darex process, since it requires high-temperature and mechanical operations and is not a universal process for all types of fuels with a chromium-containing structural material.

Data. In the carburization process, methane is passed over stainless steel at 900-1000°C. The methane is decomposed and carbon diffuses into the stainless steel, forming carbides of chromium and iron. After homogenizing for 1 hr at 1100°C, the fuel is cooled and dissolved in a mixture of nitric acid and urea. The rates of carburization as a function of temperature are shown in Fig. 9.1. Figure 9.2 shows the progressive rate of dissolution of carburized stainless steel in 3.0 M HNO₃. The dissolution rate falls off with time owing to the passivating action of nitric acid and to the decreased rate of diffusion in the later stages. A 100-mil-thick fuel plate would be dissolved in 6-10 hr. Urea is added to the dissolver solution to react with the oxides of nitrogen which form in the dissolution reaction and are believed to cause passivation.

In a series of experiments 2.5 wt % carbon was introduced into nonirradiated prototype APPR fuel samples (stainless steel-clad, sintered UO₂-stainless steel core) by passing a mixture of methane and hydrogen over the metal for 2 hr at 1000°C. The samples were dissolved in 3.0 M HNO₃ containing 0.3 M urea at a rate corresponding to about 8 hr for a full-size element. The insoluble carbide residue, about 27% of the stainless steel, was leached with boiling 10 M HNO₃ to recover any remaining uranium dioxide. Uranium losses in the solids were 0.008, 0.34, and 0.25% of the original uranium in three experiments.

9.3 Oxidation of Zirconium Fuels (R. E. Adams, R. G. Wymer)

Status. Oxidation of zirconium-containing fuels is a promising method for processing natural or slightly enriched fuels where the zirconium is present only as jacket material or as jacket and a minor (<10%) constituent of the core alloy. Uranium recovery is essentially quantitative in these cases but decreases with zirconium concentration in the alloy. The fate of plutonium is unknown. It is impractical for fuels containing ~99% zirconium, since about 15% of the uranium remains in the nitric acid-insoluble residue. Other general limitations are the same as those listed for carburization above.

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Fig. 9.1. Carbon Content as a Function of Time.

Fig. 9.2. Progressive Dissolution Rate of Carburized Stainless Steel in Nitric Acid.

Data. Oxidation^{14,34,37-39,41,42,76,67} of zirconium-containing fuels converts the zirconium to powdered insoluble oxides at rates ranging from 0.26 mg/cm²/min at 1000°C for Zircaloy-2 to ~8 mg/cm²/min at 500°C for 10% zirconium-90% uranium alloys in dynamic systems where the samples were shaken to remove oxide film continuously. The static oxidation rate of 2% zirconium-98% uranium and 7% zirconium-93% uranium alloy was very slow, ~0.015 mg/cm²/min at 400-1000°C. Under dynamic conditions, a sphere of 2% zirconium-98% uranium alloy with a diameter of about 0.4 cm was converted completely to powdered oxides in 60 min at 800°C. The oxidation rate passed through a pronounced maximum between 300 and 700°C. The uranium was recovered from the powdered oxides by leaching with nitric acid. Uranium recovery was essentially quantitative for ~10% zirconium-90% uranium alloy, but losses increased to 15% as the zirconium content of the alloy increased to ~90%. Oxidation accomplishes both inactivation of zirconium in nitric acid solutions and the removal of zirconium from the system. Oxidation was not particularly successful with niobium alloys because of excessive uranium losses, ~0.7% uranium loss for 2% niobium-98% uranium alloy.

9.4 Hydriding and Nitriding of Zirconium Fuels

Status. Hydriding has been used to convert zirconium to a nitric acid-soluble form in the Y-12 scrap recovery operations. In general, uranium recovery was quantitative for large zirconium pieces, but hydriding was not complete in the case of heavily oxidized small scrap pieces. The fate of plutonium is unknown. The rate of dissolution of the hydride in nitric acid is slow and the safety of the hydride-nitric acid system uncertain. Other general limitations are the same as those listed for carburization above.

Nitriding with nitrogen or ammonia at elevated temperatures did not successfully convert zirconium to a nitric acid-soluble form.

9.5 Sulfuric Acid and Hydrofluoric Acid Processes

Status. Stainless steel fuels are soluble in dilute (6 M) sulfuric acid. The uranium cores dissolve after addition of nitric acid to the sulfuric acid. Limitations arise through the corrosiveness of the sulfuric acid on the stainless steel dissolver, the passivation effect of traces of nitrate on succeeding stainless steel batches, the inhibiting effect (causing low throughput) of sulfate on the extraction system, and the increase in waste volume.

Zirconium fuels containing ~99% zirconium, are readily dissolved in HF in a Monel dissolver, forming a residue of UF₄. The uranium residue is dissolved by adding nitric acid to the HF solution. The solution is quickly transferred to a stainless steel tank, to avoid rapid corrosion of the Monel by the nitric acid, and aluminum is added to inhibit the corrosion effect of fluoride in subsequent processing steps. Limitations of this process are the corrosive effects of the fluoride-nitrate system in the head end and particularly in the radioactive waste system and the vastly reduced throughput of the process resulting from the dilution required to maintain zirconium, aluminum, and uranium in solution under process conditions.

Program. These processes have been demonstrated on nonirradiated fuels at Argonne¹⁰⁶ and KAPL¹⁰⁵ and will be demonstrated at the Idaho Chemical Reprocessing

Plant on irradiated fuels in FY-57 and 58. This demonstration will provide data for firm cost estimates. No work is planned on these systems at ORNL other than comparative cost evaluations. It is our opinion, however, that a development program almost equivalent to that required for a completely new process will be required to adapt the hydrofluoric acid and sulfuric acid processes to fuels other than those for which they were designed.

9.6 Electrolytic Dissolution (A. H. Kibbey, J. E. Savolainen)

Status. Electrolytic dissolution in nitric acid appears to be an excellent chemical method for dissolving all types of fuel elements, but a satisfactory dissolver has not been designed and tested. The mechanical aspects of remote operation and maintenance are particularly difficult. Results to date indicate that electrolytic dissolution is particularly applicable to stainless steel-containing fuels. Experiments with zirconium are encouraging, but completely satisfactory dissolution in a non-fluoride-containing solution has not been achieved.

Electrolytic dissolution represents a desirable problem for long-term development. Consequently, a subcontract has been let to Carter Laboratories, Pasadena, California, to study the problem. Carter Laboratories is highly qualified in the electrochemical field. Emphasis is to be placed on the engineering development of a suitable mechanical system and a laboratory study of the factors controlling anodic zirconium dissolution in aqueous systems.

Data. Stainless steel^{14,38,41,42} dissolved anodically with direct current in 10 M HNO_3 as Cr(III), Fe(III), and Ni(II) at a rate of 5 mg/cm²/min at a current density of 0.399 amp/cm². The current efficiency was 76.5% at 50°C, 77.5% at 75°C, and 78% at 90°C. Alternating current was also studied since the capital investment would be lower if rectifiers are not required. With alternating current stainless steel samples dissolved in 10 M HNO_3 at a rate of 15.5 mg/cm²/min. The current density was 4 amp/cm² and the current efficiency was 48.2%. The electrolytic dissolution rates are plotted as functions of nitric acid concentration and current density in Figs. 9.3 and 9.4. These data represent the results of controlled laboratory conditions where the current density is known and should not be extrapolated directly to large-scale equipment where the current density is a variable.

With alternating current, electrodes of zirconium^{39,41,42} and Zircaloy-2 disintegrated in 15 M HNO_3 to form a black scale, which dropped from the surface. Anodic dissolution in 3 M HCl was somewhat more successful, with large fractions of the zirconium dissolving and the remainder transferred to the solution as a fine metallic sol. Recovery of the uranium from anodically dissolved uranium-zirconium fuel element sections was poor in initial attempts. About 22% of the uranium was lost in a nonleachable form in the black solids, which have been identified by x-ray analysis as alpha-zirconium metal. As the current density increased from 0.017 to 0.27 amp/cm², the percentage of the total zirconium transferred to the solution as soluble zirconium increased from 62.1 to 96.5% (Table 9.1).

9.7 Molten Metal Dissolution (R. G. Wymer)

Status. The dissolution of enriched uranium-stainless steel (APFR) and zirconium-containing fuels in molten metals such as aluminum, zinc, tin, and

Fig. 9.3. Electrolytic Dissolution of Stainless Steel in Nitric Acid with Direct Current.

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Fig. 9.4. Electrolytic Dissolution of Stainless Steel in Nitric Acid with Alternating Current.

Table 9.1 Rate of Anodic Dissolution
of Zirconium in 3 M HCl

Current Density (amp/cm ²)	Wt. Loss per amp-hr (g)	Zr Dissolved per amp-hr (g)	% of Wt. Loss Found as Soluble Zr
0.017	1.53	0.95	62.1
0.067	1.25	0.90	72.1
0.14	1.14	0.90	78.5
0.27	0.88	0.81	96.5

magnesium has been studied as a means of converting them to a nitric acid-soluble form. In addition, the use of tin as a dissolvent and concentration agent for enriched uranium-aluminum fuels has been studied by the Metallurgy Division⁷⁷ as a possible method of reducing reprocessing costs by a pyrometallurgical technique. In this process aluminum is eliminated in the head-end step by selective precipitation.

Cost studies of the stainless steel and zirconium-metal dissolution processes showed that they are not economically competitive with alternate methods because of the large amounts of alloying metals required and the resultant decrease in plant throughput and increase in waste storage costs. No further work is planned in this system. Approximately 85% of the aluminum has been eliminated from aluminum-containing fuels in the molten tin process, but uranium recoveries have been inconsistent, varying from 76.0 to 102.0%. This process also requires a large inventory of tin. Since high-temperature pyrometallurgical processes have not been run on a large scale, it is not possible to make a precise cost evaluation of these schemes.

Data. Samples of high zirconium-uranium fuel elements^{14,36,38,39,41,42} formed an alloy with molten zinc in 5 to 10 hr at temperatures above 800°C and Zn/Zr weight ratios of 5/1 to 7/1. In tests on a proposed flowsheet for such fuel elements (Fig. 9.5), the alloying rate increased with increasing temperature and increasing Zn/Zr ratios. The resulting melt dissolved readily in boiling 8 M HNO₃ for all Zn/Zr ratios above 6/1. In several of the experiments, small amounts of solid ZrO₂ that remained after the dissolution contained several percent of the total uranium. When a small amount of magnesium was added, to give a melt with a zinc/zirconium/magnesium weight ratio of 10/2/1, the uranium loss was less than 0.5%.

High zirconium-uranium fuel elements formed alloys with molten tin and aluminum at about the same rate as with zinc, but the melts did not dissolve so completely in acid.

9.8 Aqueous Dejacketing Methods (W. E. Clark, A. H. Kibbey)

Objective. The removal of stainless steel or zirconium fuel jackets by aqueous dissolution and discharge of the solution to waste, similar to aluminum-jacket removal by caustic from conventional fuels, would have important economic advantages. This procedure would minimize head-end mechanical procedures and eliminate the inert jacket materials and jacket dissolution chemicals from the radioactive reprocessing and waste storage systems.

Status. Stainless steel jacket removal by 6 M H₂SO₄ and zirconium or Zircaloy-2 jacket removal by 14 M boiling H₂SO₄ or HF have been scouted. Initial results indicate that the dejacketing solutions dissolve small amounts of the alloy or oxide cores and probably cannot be discarded, particularly if the plutonium losses prove to be of the same magnitude as the uranium losses. Further work at full irradiation levels is required to answer this important question. If the solutions cannot be discarded, nitric acid must be added to the dejacketing solution to dissolve the cores and consequently the sulfate and fluoride ions will pass through and complicate the reprocessing system. Comparative cost estimates are under way to evaluate the feasibility of these schemes as compared to Zircex or Darex. The cases where only very thin jackets of zirconium or stainless steel are involved (and thus very little H₂SO₄ or HF is required) appear to be economically attractive.

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Fig. 9.5 Flowsheet for Fuel Element Dissolution in Molten Zinc.

Suitable metals of construction must be found since corrosion problems are severe in these dejacketing solutions. Both boiling 14 M H_2SO_4 and HF are corrosive in stainless steel and the evolution of H_2S , SO_2 , and free sulfur in the case of zirconium dissolution in 14 M H_2SO_4 is an added off-gas problem.

Monel cannot be used for zirconium-jacket removal by HF since the core must be dissolved in nitric acid in a second step. Nitric acid is extremely corrosive on Monel. The alternate is to use a stainless steel dissolver for both dissolution steps or mechanically transfer the core from a Monel tank to a stainless steel tank for a two-step dissolving. Another alternate is to use a mixture of HNO_3 - $\text{Al}(\text{NO}_3)_3$ -HF to dissolve zirconium. In this case the fluoride is complexed by the aluminum and is less corrosive to stainless steel but still maintains a reasonable dissolving rate for zirconium.

Data. Very few data are available as yet on aqueous dejacketing procedures.^{14, 18, 20, 39, 40} It has been reported¹⁰⁴ that concentrated boiling sulfuric acid may be a suitable dissolvent for zirconium cladding, and it is well known that hydrofluoric acid dissolves zirconium readily. Similarly, studies have shown that stainless steel can be dissolved in excess 6 M H_2SO_4 at an average rate of approximately 11 mg/cm²/min at 100°C.¹⁰⁵ However, no data were available on the reactivity of uranium or other core materials in these acids. This is important since the dejacketing solution could be discarded if it did not dissolve valuable materials and consequently would not complicate the extraction or waste systems. Initial studies have shown that both zirconium and Zircaloy-2 are soluble in a large stoichiometric excess of boiling 14 M H_2SO_4 at rates of 7 and 38-56 mg/cm²/min, respectively. Considerable amounts of H_2S , SO_2 , and free sulfur are evolved. In experiments with prototype fuel a 28-mil Zircaloy-2 jacket was dissolved from a 0.36-in.-dia UO_2 core along with approximately 0.2% of the uranium. In another experiment a 4-mil zirconium jacket was removed from a 0.12-in.-dia 10% molybdenum-90% uranium core with a 100% stoichiometric excess of boiling 1 M HF. The solution was filtered and 0.42% of the uranium was found in the filtrate. Apparently UF_4 was oxidized to soluble UO_2F_2 . Jacket removal experiments with boiling 6 M H_2SO_4 have not been performed, but dissolution rates of 0.03 and 0.008 mg/cm²/min were determined for uranium metal and 10% molybdenum-90% uranium alloy, respectively.

The rate of dissolution of both zirconium and Zircaloy-2 in an aqueous aluminum nitrate-fluoride-nitric acid system was higher with higher nitric acid concentrations, as shown in Table 9.2. The dissolution rate of Zircaloy-2 was essentially a linear function of the zirconium concentration of the solution and the time (Fig. 9.6). Calculated penetration rates were:

	<u>11 M HNO_3 Dissolvent</u>	<u>3 M HNO_3 Dissolvent</u>
Zirconium	5.8 mils/hr	3.3 mils/hr
Zircaloy-2	4.6	2.8

Table 9.2 Dissolution Rates of Zirconium and Zircaloy-2
versus $\text{KF-HNO}_3\text{-Al(NO}_3)_3$ and $\text{HF-HNO}_3\text{-Al(NO}_3)_3$

Time (hr)	Zirconium		Zircaloy-2	
	Dissolution Rate (mg/m/cm ²)	Zr in Solution (M)	Dissolution Rate (mg/m/cm ²)	Zr in Solution (M)
Dissolvent: 11 M HNO_3 , 0.35 M $\text{Al(NO}_3)_3$, 0.3 M KF				
1	1.74	0.026	1.64	0.021
2	1.26	0.046	1.32	0.036
	1.50 avg.			
3	1.18	0.062	1.14	0.049
			1.37 avg.	
4	0.94	0.073	0.89	0.058
5	0.88	0.081	0.67	0.067
Dissolvent: 3 M HNO_3 , 0.7 M $\text{Al(NO}_3)_3$, 0.5 M HF				
1	1.16	0.017	1.05	0.014
2	0.97	0.032	0.97	0.026
3	0.93	0.045	0.93	0.037
4	0.76	0.057	0.86	0.044
5	0.77	0.068	0.81	0.052
6	0.72	0.076	0.73	0.058
7	0.71	0.085	0.69	0.065
8.5	0.64	0.095	0.60	0.073
	0.84 avg.		0.83 avg.	

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9.9 Acid Dissolution of Fuel Cores (W. E. Clark, A. H. Kibbey)

Objective. Core alloys or oxides must be dissolved in acids prior to solvent extraction. Direct acid dissolution would be used following jacket removal by mechanical or chemical methods, or after mechanical chopping to expose core materials.

Status. Fuel cores composed of uranium-molybdenum, uranium-silicon, uranium-aluminum, plutonium-aluminum, UO_2 , $\text{UO}_2\text{-PuO}_2$, or uranium metal either are soluble in nitric acid or the uranium can be quantitatively recovered by leaching with nitric acid.

Sintered alloys of stainless steel and UO_2 require sulfuric acid followed by nitric acid or a mixture of hydrochloric and nitric acids for dissolution when stainless steel is the major phase.

Alloys of zirconium-uranium and probably niobium-uranium cannot be directly dissolved in nitric acid or dilute aqua regia because of explosive reactions of the acid with the intermetallic compounds. The presence of fluoride in the mole ratio $\text{F/Zr} = 4/1$ prevents explosions. A mixture of $\text{HNO}_3\text{-Al}(\text{NO}_3)_3\text{-HF}$ is an effective dissolving agent.

The Thorex process dissolvent, 13.0 M $\text{HNO}_3\text{--}0.05$ M HF , can be used to leach thorium from chopped zirconium-jacketed thorium fuels. The zirconium slowly dissolves, but does not interfere with the core dissolution.

The above conclusions apply only to nonirradiated fuel. The effect of the extremely high, 10,000 Mwd/ton, irradiations now proposed on fuel solubilities is not known. For example, the solubility of plutonium oxide formed in oxide fuels is uncertain.

Data. Dissolution rates^{14-20,39,40,45} of all alloys tested were satisfactorily fast in 5 M $\text{HNO}_3\text{--}2$ M HCl . In boiling 8 M HNO_3 the rates of 2 and 5% niobium alloy were satisfactorily fast, but the rate for 15% niobium alloy was too slow, 0.3 mg/cm²/min, for process use. When leached with aqua regia, the insoluble residues from molybdenum alloys retained almost no uranium, the niobium alloy residues retained 0.1 to 1% of the uranium, and the zirconium alloys retained 1 to 15% of the uranium. Losses appeared to increase slightly with the niobium content and markedly with the zirconium content, but in general were non-reproducible. Uranium was quantitatively leached from uranium-silicon alloys; the residue of silica looked like a sugar cube (Table 9.3).

Dissolution of molybdenum-uranium alloy in nitric acid is complicated by the insolubility and precipitation of molybdic acid. A solution obtained by dissolving 12% molybdenum--88% uranium alloy was saturated with molybdenum when it contained only 5 g of uranium per liter, which is too low a uranium concentration for efficient solvent extraction processing. Solvent extraction feed that contained about 200 g of uranium per liter was prepared by dissolving the alloy in 11 M HNO_3 to a uranium concentration of 260 g/liter. The molybdic acid that precipitated was filtered off and dissolved in caustic, the caustic solution was centrifuged to separate the uranium solids that had been occluded in the molybdic acid precipitate, and the uranium solids were dissolved in acid and recycled. A flowsheet for this process is shown in Fig. 9.7.

Table 9.3 Dissolution Rates of Various Core Materials
in Boiling Simulated Process Solutions

Alloy Composition (%)					Dissolution Rate (mg/cm ² /min)			
					H ₂ SO ₄		HNO ₃	Aqua Regia
					6 M	14 M	8 M	2 M HCl - 5 M HNO ₃
U	Zr	Nb	Mo	Si				
100					0.0316	> 0.258		
97.9	2.1							7.61
92.5	7.5							9.33
90	10							17.88
85	15							9.46
80	20							6.80
98		2					6	10.95
95		5					4	9.06
90.3		9.7						13.58
85		15					0.3	6.51
95	4.5	0.5						12.33
93.3	5.3	1.3						14.68
98			2					12.56
90			10		0.008		85-108 ^a	
~ 99	0.41	0.12	0.22					32.70
99.5				0.5	0.043		58.15 ^b	7.50
99				1.0	0.064		76.74 ^b	
98				2.0	0.052	0.11	22.95 ^b	

^a Rates determined over a period of 13 to 93 min.

^b Initial rate drops off sharply with formation of SiO₂ coating on surface.

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Fig. 9.7. Schematic Flowsheet for Processing Uranium-Molybdenum Fuels.

9.10 Corrosion of Materials of Construction (W. E. Clark)

Objective. In processes involving corrosive reagents, the selection of proper container materials is of prime importance. Because of the combination of peculiarly severe conditions encountered in both Zircex and Darex processes, a thorough investigation of the corrosion of possible materials of construction is an absolute necessity. The bulk of this program is being carried out by the Battelle Memorial Institute under an ORNL subcontract. A minimum amount of survey work has been done at ORNL.

Status and Data. In addition to metallic materials, industrial glass and glass-lined equipment is under consideration for use in parts of the equipment which will be relatively free from mechanical shock. The "corrosion" rate of Pfaudler glass, for example, has been determined to be of the order of 1-2 mils/year in Darex type dissolver solutions. The stability of glass to irradiation levels of the order expected to be encountered is presently unknown but will be determined in the near future.

Of the metals which have been tested thus far, only the special high-temperature cobalt alloys, such as S-816, appear to offer real promise as construction materials for a combination hydrochlorinator-dissolver in the Zircex process. Scouting tests on S-590, Haynes-25, and Vitallium (Haynes-21) indicate that these materials may be more inert than S-816. In higher acid concentrations (3 M H^+ and above), Carpenter 20 and 20S may possibly qualify. If separate vessels are to be used for the hydrochlorination and dissolving steps, there is a considerably wider choice of materials. Inconel, for example, does well in gaseous $HCl-H_2$, but corrodes rapidly in the aqueous nitric acid-uranium chloride solutions encountered in the Zircex dissolution step. Titanium and tantalum, on the other hand, show negligible corrosion rates in dissolver solution, but fail completely and rapidly under hydrochlorination conditions. Tantalum suffers hydrogen embrittlement at temperatures as low as $400^\circ C$, while titanium is destroyed by a combination of embrittlement and hydrochlorination.

Owing to the general similarity of the Zircex dissolver solutions to the Darex, the testing of materials in Darex dissolver solutions has just begun, and from the results of the Zircex dissolver tests it appears highly probable that both titanium and tantalum will prove satisfactory as a material of construction for the Darex dissolver. There appears to be no chance for hydrogen embrittlement in the Darex dissolver, but this possibility will, nevertheless, be considered. Some of the other metals now being tested may also prove satisfactory for Darex service.

Data from the tests to date are listed in Tables 9.4 and 9.5. The corrosion data of cobalt alloy S-816 as a function of acid concentration are presented in Figs. 9.8 and 9.9.

Table 9.4 Laboratory-scale Corrosion Tests for
Zircex Dissolver Material

All specimens completely submerged in liquid at boiling temperature.

Metal	Corrosion Rates (mils/month)		
	0.5 M HNO ₃	3.0 M HNO ₃	5.0 M HNO ₃
	0.4 M UO ₂ ⁺⁺	0.4 M UO ₂ ⁺⁺	0.4 M UO ₂ ⁺⁺
	1.2 M Cl ⁻	1.2 M Cl ⁻	1.2 M Cl ⁻
Carpenter 20	79.7	1.96	2.01
Carpenter 20S	74.1	2.10	3.76
Hastelloy C	7.05	15.8	24.6
Monel	200	359	495
Haynes 25	1.52	1.08	2.60
Vitallium	2.04	0.81	1.68
S-590	2.64	3.07	5.10
S-816	3.72	6.67	9.09

Table 9.5 More Extensive Corrosion Tests for Zircex Dissolver Material

Tests carried out under reflux, 100-122°C

Metal	Specimen Position	Cumulative Corrosion Rate (mils/month) ^a										
		0.5 M HNO ₃ 0.4 M UO ₂ ⁺⁺ 1.2 M Cl ⁻			3 M HNO ₃ 0.4 M UO ₂ ⁺⁺ 1.2 M Cl ⁻			5 M HNO ₃ 0.4 M UO ₂ ⁺⁺ 1.2 M Cl ⁻			15 M HNO ₃ 0.4 M UO ₂ ⁺⁺ HCl bubbled through	
		160 hr	330 hr	660 hr	156 hr	506 hr	670 hr	160 hr	330 hr	170 hr	325 hr	490 hr
S-816	Vapor	0.381	0.192	0.102	0.301	0.156	0.134	1.40	---	1.64	1.76	---
	Interface	0.431	0.228	0.129	0.515	0.295	0.276	1.76	---	2.00	2.37	---
	Liquid	0.299	0.177	0.100	0.564	0.350	0.344	2.15	---	1.83	2.73	---
Illium R	Vapor	2.38	1.29	---	1.57	0.613	---	11.4	---	5.34	40.4	---
	Interface	53.77	27.6	---	10.5	18.9	---	92.1	---	2.44	8.07	---
	Liquid	55.46	28.9	---	13.0	18.5	---	106.0	---	2.65	4.49	---
Hastelloy B	Liquid (3 hr exp)	435.9	---	---	11,174	---	---	---	---	---	---	---
					7,141	---	---	---	---	---	---	---
Nickel "A"	Liquid (4 hr exp)	665.0	---	---	---	---	---	Failed (<3 hrs)	---	---	---	---
304 ELC	Vapor	---	---	---	181	---	---	---	---	6.61	16.1	---
	Interface	---	---	---	2420	---	---	---	---	1.34	6.69	---
	Liquid	---	---	---	177	---	---	---	---	1.04	0.81	---
Inconel	Liquid	---	---	---	4550	---	---	---	---	---	---	---
Titanium	Vapor	0	g	g	g	---	0.004	---	0.145	g	0.064	0.072
	Interface	g	g	0.002	0.029	---	0.005	---	0.028	0.015	0.177	0.160
	Liquid	0	g	g	0.013	---	0.002	---	0.009	0.034	0.535	0.476
Tantalum	Vapor	g	g	g	g	---	0.006	---	g	g	g	g
	Interface	g	g	g	g	---	0.002	---	g	g	g	g
	Liquid	g	g	g	g	---	0.0001	---	0	g	g	0.001

^a g indicates slight weight gain. Corresponding corrosion rates have not yet been calculated exactly but are very small in every case.

Fig. 9.8. Corrosion of Cobalt Alloy S-816 as a Function of Acid Concentration in Zircex Dissolver Solution.

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Fig. 9.9. Corrosion of Cobalt Alloy S-816 in HCl-HNO_3 as a Function of Acid Concentration.

10.0 SOLVENT EXTRACTION APPLICATIONS

J. R. Flanary, J. H. Goode

10.1 Objective

Major effort has been placed on the development of adequate solvent-extraction systems for processing reactor fuels susceptible to conversion to aqueous nitrate solutions by the Zircex or Darex processes. Continued study of these systems is expected to yield chemical flowsheets, and auxiliary data, whose performance will have been proved by laboratory-scale operation with fully irradiated fuel specimens. Specifically, solvent-extraction chemical development must include investigation of (1) first solvent extraction cycle, (2) additional cycles, (3) solvent and diluent stability toward radiation, and (4) investigation of other solvents such as the amines and alkyl phosphates as indicated by the work of K. B. Brown and others at ORNL.

10.2 Status

Based upon past experience and the results gained thus far, there appear to be no formidable problems associated with the solvent-extraction reprocessing of uranium-stainless steel fuels except interference from radiation-induced impurities generated in process. A limited evaluation of this problem will be attempted when fully irradiated APPR specimens are processed in the mini-mixer-settler facility. Solvent-extraction work with the zirconium-containing fuels has not progressed to the point that a reasonable evaluation can be made. The zirconium content of the feed solutions is expected to be very low after the Zircex head-end removal of zirconium. Consequently, no unusual problems are anticipated in this system.

Presently available solvent irradiation data indicate that Purex type processes can probably handle power reactor fuels at the proposed levels of irradiation after suitable decay times to eliminate iodine and lanthanum. However, a great deal more basic information (theoretical, empirical, and operating) is required. The effects on solvents of processing short-decayed fuel will require the development of new solvent recycle and cleanup methods.

10.3 Data

Army Package Power Reactor Flowsheet. Because of the immediate availability of highly irradiated APPR fuel specimens, initial data have been obtained from studies of the uranium-stainless steel fuel types.^{14-20,37-42} Samples of non-irradiated uranyl nitrate-stainless steel-nitric acid solutions were prepared over a wide concentration range, and important physical properties such as specific gravity, relative viscosity, and freezing and boiling points were determined. These data help define the stable composition range for solvent-extraction reprocessing of uranium-stainless steel fuel solutions (Figs. 10.1-10.3).

Since the dissolution of APPR fuel yields a low-uranium (5 g/liter) high-stainless steel (63 g/liter) feed, 5% TBP was chosen as an optimum solvent concentration. Uranium extraction coefficient data obtained by the batch equilibration method predicted a satisfactory solvent-extraction system for uranium recovery. A 6.5-hr mini-mixer-settler run was made with the tentative flowsheet indicated

Fig. 10.1. Specific Gravity of SS-HNO₃-Uranium Solutions as Function of Concentration.

Fig. 10.2. Relative Viscosity of HNO₃-Stainless Steel-Uranium Solutions as Function of Uranium and HNO₃ Concentration.

Fig. 10.3. Uranium-Stainless Steel (304) Feed Solution Freezing Points for 2 M HNO_3 .

below to demonstrate recovery of enriched uranium from APPR fuel solution.

APPR Chemical Flowsheet,
First Solvent-extraction Cycle

Aqueous feed (100 vol): 5 mg U per milliliter, 3 M HNO_3 , 46 mg Fe per milliliter, 11 mg Cr per milliliter, 5 mg Ni per milliliter

Aqueous scrub (20 vol): 3 M HNO_3 , 0.75 M $\text{Al}(\text{NO}_3)_3$, 0.01 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$

Solvent (83 vol): 5% TBP in Amsco 125-82

Aqueous strip (83 vol): 0.01 M HNO_3

A total of 8 extraction, 8 scrub, and 8 strip stages (mixer-settler) were used. The results indicated that about 4 theoretical extraction stages and 2 strip stages would be required, based on an assumed 50% stage efficiency in the mixer-settlers, to reach uranium losses of approximately 0.01%. Figures 10.4 and 10.5 show the mini-mixer-settler facilities now in use.

Simulated aqueous wastes from the APPR flowsheet were concentrated by evaporation and freezing points determined. Solution concentrated 3 to 1, from 53 g of stainless steel per liter and 3 M HNO_3 to approximately 169 g of stainless steel per liter and 3.5 M HNO_3 , was metastable at room temperature. Solution concentrated 4 to 1 crystallized on cooling to room temperature (22°C).

APDA Flowsheet. Dissolution of the APDA Radial Blanket (stainless steel-clad depleted uranium) by the Darex process is expected to yield a feed solution containing approximately 1 M uranium, 1 M stainless steel, and 1 M HNO_3 . Such feed could be processed in a Purex plant for plutonium and uranium recovery. A feed of greater concentration would be unstable as regards salt precipitation at normal operating temperatures. In batch countercurrent experiments simulating the extraction-scrub contactor in the first solvent-extraction cycle, the following solutions were used:

Aqueous feed (40 vol): 215 g U and 50 g stainless steel per liter,
1 M HNO_3 , 0.01 M NaNO_2 , Pu(IV) tracer

Aqueous scrub (20 vol): 3 M HNO_3

Solvent (100 vol): 30% TBP in Amsco 125-82

Results indicated that the uranium loss was reduced to 0.01% with about 2

Fig. 10.4. Shielded Mini-Mixen-Settler Facility.

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Fig. 10.5. Mini-Mixen-Settler Facility.

extraction stages, whereas about 4.5 extraction stages were needed to reduce the plutonium loss to 0.01%.

Consumers Public Power Reactor Flowsheet. Fuel from the Consumers Public Power reactor, after Darex treatment, yields a stable feed solution containing 320 g of uranium and 28 g of stainless steel per liter and 1 M HNO_3 . Fig. 10.6 shows the Purex-type head-end (decontamination) flowsheet devised for this fuel. Initial tests of this flowsheet, based on uranium and plutonium recovery, indicate it to be satisfactory.

Solvent Radiation Damage. Radiation damage to process reagents is important in reprocessing nuclear reactor fuels by solvent-extraction, especially with short-decayed fuels where fission product radiation is very intense. The magnitude and nature of chemical changes induced by radiation may affect the performance, and perhaps the feasibility, of certain solvent-extraction processes designed to recover fissionable materials. It is estimated that the organic solvent will receive 2-4 watt-hr/liter exposure per pass through the primary extraction contactor for fuel irradiated to 5000-10,000 Mwd/ton and decayed 10 days. Therefore, extensive studies of the radiation damage sustained by the solvent (tributyl phosphate) and diluent (Amsco 125-82) have been undertaken, using Co^{60} as a gamma radiation source.

It is known that the diluent purity is important in solvent-extraction operations. The presence of easily oxidizable substances, aromatics, and unsaturates, partly by radiation-induced reactions, leads to formation of colored complexes, emulsions, and interfacial solids which retain fission products and transuranics. Consequently, there is a continuing search for a more "chemically pure" diluent.

Ultraviolet and infrared examinations of irradiated diluent have indicated that unsaturates formation may be the primary form of radiation damage. This observation has been verified by iodine number determinations of selected, relatively pure, diluents (Amsco 125-82, Deobase, and n-dodecane) exposed to Co^{60} gamma dosages up to 68 watt-hr/liter (approximately 1.76×10^7 r). Table 10.1 and Fig. 10.7 show the increase in unsaturates formation with increased dosage.

Samples of Amsco 125-82 exposed to 477 and finally to 1920 watt-hr/liter showed a decreasing rate of unsaturates formation as damage occurred. The maximum iodine number reached was approximately 15.

It is postulated that double bonds are likely sites of iodine and ruthenium addition, oxidation, and nitration. Free radicals may also undergo similar reactions plus addition of hydrocarbon chains, polymerization, etc.

Massive doses of Co^{60} radiation (477 watt-hr/liter) to TBP--Amsco 125-82 mixtures, both wet and dry, have yielded DBP, MBP, waxy polymers, emulsifiers, and unknown compounds formed by combination of the degradation products of both diluent and TBP. The uranium retention by these irradiated mixtures has been found to be several times greater than that attributed to DBP formation.

Although the DBP and MBP are easily removed from the irradiated mixture by alkaline washing, other radiation-induced impurities remain. Vacuum distillation of such solvent appears to be a fairly efficient method of recovery. About 90%

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Fig. 10.6. Solvent Extraction Flowsheet for Processing Consumers Public Power Fuel.

Table 10.1 Formation of Unsaturation in Hydrocarbon Diluents
as a Function of Radiation Dosage

Irradiation (watt-hr/liter)	Iodine Number		
	<u>n</u> -dodecane	Deobase	Amsco 125-82
0.0	0.0	1.15	2.40
11.4	---	---	2.65
22.7	0.88	---	3.10
45.7	1.51	2.92	4.12
68.2	---	3.55	4.85

Fig. 10.7. Formation of Unsaturates in Hydrocarbon Diluents as a Function of Irradiation Dosage.

of the TBP and diluent can be recovered in pure form by this method.

Subcontract negotiations are in progress with Stanford Research and Georgia Institute of Technology to institute studies on the chemistry of radiation damage to organic solvents and the identification of degradation products. From this work, it is hoped to reach a better understanding of the complicated mechanisms of radiation damage so that, ultimately, deleterious process effects resulting from radiation-degraded solvent may be obviated by (1) properly modified chemical and operating conditions or (2) discovery of new solvents possessing high resistance to radiation.

11.0 THE HERMEX PROCESS
O. C. Dean, B. H. Morrison

11.1 Objective

The Hermex process is a zero valence state process being developed on a long-range basis. It has the potential of achieving the same results as the high-temperature pyrometallurgical processes proposed for fast reactors. It utilizes mercury as a dissolution and recrystallization agent for decontaminating spent uranium fuels and recovering scrap uranium and thorium metal. The use of mercury to degrade and leach the uranium from refractory alloys of uranium is also under investigation.

11.2 Status

Fission products have been removed from long- and short-decayed irradiated uranium on a 20-50 g uranium batch basis. Decontamination factors have been better than for high-temperature pyrometallurgy methods, but less than for solvent-extraction and volatility methods. Unirradiated natural uranium also has been purified. The results obtained have been from runs in glass dissolver apparatus. Since hot solutions of uranium in mercury attack glass, it is probable that the oxides in the glass may be reducing the ultimate purification obtainable. Stainless steel apparatus has been built in which the oxygen supply can be controlled to evaluate this possibility. Uranium losses in each step are not known with confidence.

11.3 Data

Dissolving rates and solubilities for uranium in mercury and amalgams at 356°C and 1 atm have been determined. It has been shown that uranium-zirconium and uranium-molybdenum alloys may be dissolved at practical rates when the alloying metal content is not above 10%. A 1-kg uranium partially continuous stainless steel dissolver and filter unit has been constructed and is under test. The continuous removal of mercury and subsequent melting of uranium to form massive metal has been demonstrated on a 100-g uranium scale.^{14-20, 35-44}

At this early stage in the development of Hermex, it appears that for uranium, thorium, alloys high in uranium, and uranium-molybdenum alloys the chances for success are good. It gives decontamination higher than that obtained in conventional pyrometallurgy. The waste streams may contain small amounts of uranium as oxides to be recovered by solvent extraction, but it is thought that the savings will be appreciable, since the bulk of the metal will be on short cycle and on a low inventory basis. For the refractory alloys, a planned alternate is to hydride or heat with metal vapors as a head-end treatment to decompose the alloy and free the uranium before leaching with mercury.

The steps in mercury processing of metals are shown in Fig. 11.1. Wastes from the dissolver are solid slag which is not wetted by mercury and may be floated off. The process, with the exception of filtration and final melting, has been operated continuously. Difference in free energies of formation of oxides of contaminants of interest are shown in Table 11.1, and the uranium-mercury phase diagram is shown in Fig. 11.2.

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Fig. 11.1. Schematic Flowsheet for the Hermex Process.

Table 11.1 Free Energies of Reaction in the
Hermex System at 633° K

Negative		Positive	
M	ΔF	M	ΔF
La	-15	Pu	+4
Nd	-12	Nb	+32
Ce	-14	Ru	+102
Sr	-9	Cs	+65
Zr	-1

Fig. 11.2. The System U-Hg Showing Critical Alloys. (From: AERE M/R 1208, B. R. T. Frost).

The results of studies of the rate of solution and saturation solubilities for uranium in mercury and various amalgams are shown in Table 11.2. The solubility of uranium at 650°C and 23 atm was shown to be at least 17 atom %, and the precipitated species was uranium metal rather than UHg_4 as at 350°C and below. Zirconium-uranium alloys, <10% zirconium, dissolve at a practical rate as do uranium-molybdenum alloys and thorium, but high-zirconium alloys are practically insoluble from 356°C and 1 atm to 800°C and 103 atm.

Data on the purification of normal scrap uranium by Hermex are shown in Table 11.3 and Figs. 11.3-11.5, and the decontamination of uranium irradiated in the ORNL Graphite Reactor is shown in Table 11.4. Fig. 11.6 shows the type 347 stainless steel apparatus in which 50-g scale equilibrations are being carried on to determine the reason for and extent of decontamination and uranium losses in each step. Fig. 11.7 is a schematic drawing of the vacuum retort and uranium melting furnace. Fig. 11.8 shows the 1 kg U/day partially continuous stainless dissolver and filter apparatus.

Table 11.2 Dissolution Rate and Solubility of Uranium in Mercury and Alangams

Solvent	Uranium Dissolution Rate ^a (mg/cm ² /min)	Solubility at 356°C (wt %)	Dissolution Rate Constant ^b (g Hg/cm ² /min)
Hg	19.5	1.12	2.2
Na(Hg), 0.3 wt %	5.0	0.50	2.5
Mg(Hg), 0.1 wt %	18.7	6.50	2.5
0.3 wt %	6.7 ^c	15.0	---
0.5 wt %	10.0 ^c	---	---
Bi(Hg), 1.5 wt %	1.36	8.80	0.02

^aBased on 135 g of solvent and 20 cm² uranium surface area.

$$\frac{dc}{dt} = \frac{ks}{m} (C_s - C)$$

where C = uranium concentration in moles/1000 g Hg; C_s = saturation concentration in moles U/1000 g Hg; s = uranium surface area in cm²; t = time in minutes; and m = mass of Hg or amalgam in grams.

^cRate data questionable because of frothing during dissolution.

Table 11.3 Spectrographic Analysis of Fernald Scrap Uranium

Element	Contamination (ppm)	
	Before Processing	After Processing
Al	140	5
B	---	6
Ca	318	5
Cu	140	14
Fe	204	7
Mg	6	0.007
Mn	13	0.03
Ni	---	4
Si	4720	150

Fig. 11.3. Photomicrograph, Fernald Scrap Uranium as Received.

Fig. 11.4. Photomicrograph, Fernald Scrap Uranium Processed by Hermex.

Fig. 11.5. Photomicrograph, Argonne Electrolytic Uranium.

Fig. 11.6. Stainless Dissolver and Filter for Small Scale Decontamination at One Atmosphere Pressure for the Hermex Process.

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Fig. 11.7. Metal Recovery Vacuum Retort and Furnace for the Hermex Process.

Fig. 11.8. One-Kilogram Uranium Semicontinuous Dissolver and Filter for the Hermex Process.

12.0 VOLATILITY APPLICATIONS - DISSOLUTION STUDIES

J. E. Savolainen, R. G. Wymer, L. M. Ferris

12.1 Objective

The objective of the fused salt Dissolution-Volatility program is to determine optimum conditions for the dissolution of fuel elements in fused salt solvents so that the volatility process can be used as a power reprocessing method. The data obtained are intended to provide a basis for design and operation of bench-scale and pilot plant dissolvers. Current effort is centered on fluoride salts as solvents for enriched uranium fuel elements containing zirconium or stainless steel. However, investigation of chloride or mixed chloride-fluoride solvents as a head-end treatment for a fluoride or chloride volatility process and the development of methods for the recovery of plutonium by volatility are also planned.

In the volatility process^{10,47-54,65} the fused fluoride salt containing the dissolved fuel is treated with gaseous fluorine to recover the uranium as volatile UF_6 . The bulk of the fission products remains in the melt. Further decontamination is achieved by sorption and desorption of the UF_6 from solid NaF beds. Decontamination factors demonstrated in laboratory-scale equipment have been very high.

A pilot plant will be in operation in late FY-1957. Only the dissolution step for fuel in fused salts is covered in this report.

12.2 Status

Suitable conditions have been determined for the dissolution of fuel elements in molten NaF-ZrF₄. Similar experiments with LiF-NaF-ZrF₄ as the solvent are in progress. At the temperatures of interest, a thricefold increase in the uranium concentration per batch is attainable if LiF-NaF is used as the solvent.

The possibility of reprocessing stainless steel-clad fuel elements by fluoride volatility has been surveyed. This scheme appears feasible with NaF-ZrF₄ (53-47 mole %) as the solvent, provided that a suitable material of construction is available. The possibility of a higher performance solvent still exists.

Plutonium separation and recovery by chloride volatilization has also been surveyed and does not appear feasible.

12.3 Data

Table 12.1 contains a summary of data on dissolution of zirconium in NaF-ZrF₄ and LiF-NaF-ZrF which are saturated with HF. All the rates listed correspond to an HF utilization efficiency of ~15%. The highest initial rates are obtained for melts rich in NaF or NaF-LiF. That is, the rates decrease as the limit of ZrF₄ solubility is approached. Melts containing LiF consistently give higher rates under comparable conditions. The temperature dependence of the rates is apparent.

Initial dissolution rates for type 347 stainless steel in the same solvents are listed in Table 12.2. Higher rates are again found for solvents containing LiF. A slight decrease in rate is observed at each temperature as the limit of

solubility of ZrF_4 is reached. This observation agrees with that expected from the higher solubility of the structural metal fluorides in NaF- or NaF-LiF-rich systems.

Table 12.1 Zirconium Dissolution Rates as a Function of Solvent Composition and Temperature

Solvent	Composition (mole %)	Temperature (°C)	Initial Dissolution Rate ($\text{mg}/\text{cm}^2/\text{min}$)
NaF- ZrF_4	65-35	600	8.3
NaF- ZrF_4	50-50	600	4.2
NaF- ZrF_4	40-60	600	0.9
NaF- ZrF_4	50-50	700	5.2
NaF- ZrF_4	50-50	800	9.2
LiF-NaF	57-43	700	13.2
LiF-NaF- ZrF_4	35-27-38	600	5.5
LiF-NaF- ZrF_4	35-27-38	700	8.3
LiF-NaF- ZrF_4	26-19-55	600	1.5
LiF-NaF- ZrF_4	26-19-55	700	5.8

Table 12.2 Type 347 Stainless Steel Dissolution Rates
As a Function of Solvent Composition and Temperature

Solvent	Composition (mole %)	Temperature (°C)	Initial Dissolution Rate (mg/cm ² /min)
NaF-ZrF ₄	50-50	600	0.1
NaF-ZrF ₄	50-50	700	1.4
NaF-ZrF ₄	50-50	800	1.8
NaF-LiF	43-57	700	3.4
NaF-LiF-ZrF ₄	27-35-38	600	1.0
NaF-LiF-ZrF ₄	27-35-38	700	2.0
NaF-LiF-ZrF ₄	19-26-55	600	0.2
NaF-LiF-ZrF ₄	19-26-55	700	2.0

13.0 DESIGN ENGINEERING

E. J. Frederick, C. E. Guthrie, A. R. Irvine,
E. L. Nicholson, W. G. Stockdale, J. W. Ullmann

Design engineering for the ORNL Power Reactor Fuel Reprocessing Program will provide support for chemical and engineering scale development work and for the ultimate design and operation of a completed multipurpose pilot plant.

13.1 Objectives

The objectives of the engineering subprogram are:

1. To assist in and keep constant surveillance over the chemical and engineering development programs so that data necessary for pilot plant design are obtained in time for preparation of the pilot plant design criteria.
2. To design equipment for high-activity-level laboratory chemical development and to assist in the design and development of full-scale plant equipment components.
3. To undertake specific design and cost studies such as equipment criticality design, equipment process interchangeability, pilot plant building shielding and arrangement, and alternate process cost comparisons, and general studies such as carrier design and fuel shipping, reprocessing capacity vs. fuel availability studies, and waste storage costs. These studies are important both in the preparation of pilot plant design criteria and in advancing the general understanding of reactor fuel processing problems.
4. To prepare design criteria for a multipurpose pilot plant.

13.2 Status of Engineering Subprogram

Considerable work, including the preparation of chemical and engineering flow-sheets, equipment design, and building layouts for a Power Reactor Fuel Reprocessing Pilot Plant, has been done. Reprocessing cost estimates for most of the specific power reactor proposals received by the AEC were prepared for processing in a plant at ORNL, assuming the use of processes discussed in this report. Cost studies for multipurpose plants and for individual plants and cost comparisons of the Darex vs. and Zircex processes have been made. A multipurpose plant preliminary design and cost estimate was prepared for the Idaho Reprocessing Meeting in January 1956.¹⁰

Design of radioactive head-end and solvent-extraction laboratory equipment and pilot plant prototype plant components for nonradioactive engineering evaluation is being carried on.

Assistance is being given to the development groups to assist in their experimental programs. Preliminary evaluations are being made on alternate processes such as HF or H₂SO₄ de jacketing and comparing them with presently preferred processes such as Zircex and Darex. Fuel specimens, both unirradiated and irradiated, are being procured for the development programs.

14.0 ENGINEERING DEVELOPMENT AND SUPPORTING PROGRAMS AT ORNL

The development program described in the previous sections is aimed primarily at the determination of adequate chemical process and equipment conditions for reactor fuels. In addition to this "main line" effort, supporting general studies and development of engineering equipment are being carried on. These are:

1. Metal Recovery Plant Operation
2. In-line Instrumentation
3. Excer-Fluorox Process
4. Metallex Process
5. Fused Salt-Volatility Pilot Plant
6. Thorex Process Pilot Plant
7. Waste Studies
8. Extraction Reagent Performance
9. Ion Exchange Studies
10. Volatility Studies
11. Chemical Engineering Research Studies
12. Equipment Decontamination Studies
13. Economic Studies
14. Feed Materials Processing
15. Hope Project
16. Neptunium Process Development
17. Americium Recovery
18. Isolation Development

15.0 BIBLIOGRAPHY

The following bibliography is arranged under two headings: (1) reports by ORNL personnel (present and former) and (2) reports from other sites. One exception should be noted, namely, that references 6, 7, 8, and 13 are of non-ORNL origin but are put in the first group so that all references to Part I (1-13) of this report can be kept together.

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APPENDIX I

TABULATION OF EXISTING, APPROVED,
AND PROPOSED AMERICAN AND FOREIGN REACTORS

For the last 18 months we have been issuing, for our own use, a reactor list on approximately a bimonthly basis. This list contains reactor name, designer, location, power (both heat and electricity), anticipated completion date, and estimated annual discharge load. The December 1956 revision of this list is given in the following appendix for general reference.

POTENTIAL FUEL REPROCESSING

Reactor	Designer	Location	Heat (Mw)	Electric (Mw)	Comple- tion Date	Estimated Annual Processing		
						(kg U ²³⁵)	(metric tons U)	(metric tons Th)
CIVILIAN POWER REACTOR PROGRAM								
ARBOR	Argonne	Arco, Idaho	~ 200	--	1959	?	?	--
BORAX-4	Argonne	Arco, Idaho	15	3	1957	20	--	--
EBR-1	Argonne	Arco, Idaho	1.4	0.2	1957	?	?	--
EBR-2	Argonne	Arco, Idaho	62	18	1958	60	1	--
EDWR	Argonne	Lemont, Ill.	20	5	1957	--	2	--
GCRE	Aerojet-General	Arco, Idaho	2	0.5	1958	?	--	--
HRT	ORNL	Oak Ridge, Tenn.	5	0.3	1957	4	--	--
LAMPRE-1	Los Alamos	Los Alamos, N. M.	1	--	1959	? ^a	--	--
LAMPRE-2	Los Alamos	Los Alamos, N. M.	15	--	?	? ^a	--	--
LAMPRE-1	Los Alamos	Los Alamos, N. M.	2	--	1956	2	--	--
LAMPRE-2	Los Alamos	Los Alamos, N. M.	1	--	1956	1	--	--
LAMPRE-3	Los Alamos	Los Alamos, N. M.	?	?	?	?	--	--
LMFRE	Babcock & Wilcox	Upton, N. Y.	5	--	1959	?	--	?
OMRE	Atomics Int., NAA	Arco, Idaho	16	--	1958	?	--	--
PRP (EPFR)	General Electric	Richland, Wash.		--	1960	? ^a	3	--
PWR	Westinghouse	Shippingport, Pa.	264	60	1957	130	15	--
SRE	Atomics Int., NAA	Santa Susana, Cal.	20	6.5	1957	--	2	--

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^a Plutonium alloy

<u>Reactor</u>	<u>Designer</u>	<u>Location</u>	<u>Heat (Mw)</u>	<u>Electric (Mw)</u>	<u>Comple- tion Date</u>	<u>Estimated Annual Processing</u>	<u>(metric</u>	<u>(metric</u>
						<u>(kg U²³⁵)</u>	<u>tons U)</u>	<u>tons Th)</u>
<u>CIVILIAN POWER REACTOR PROGRAM, continued</u>								
TBR	ORNL	Oak Ridge, Tenn.	65	16	1961	--	--	3
WGRE	General Electric	Richland, Wash.	?	?	1959	?	?	--
			(819)	(110)		(217)	(23)	(3)
<u>POWER DEMONSTRATION REACTOR PROPOSALS</u>								
APDA - Detroit Edison	PRDC	Monroe, Mich.	300	100	1960	1500 ^b	35	--
Carolina-Virginia NPA	Stone & Webster	North Carolina	?	?	?	?	?	--
Chugach Elec. Assn.	Nuclear Dev. Corp.	Anchorage, Alaska	37	10	1962	--	6	--
City of Holyoke	Ford Instrument	Holyoke, Mass.	44	15	1961	60	--	--
City of Orlando	Babcock & Wilcox	Orlando, Fla.	~ 120	~ 30	1961	?	--	?
City of Piqua	Atomics Int., NAA	Piqua, Ohio	45	12	1960	--	3	--
Commonwealth Edison ^c	General Electric	Morton, Ill.	620	180	1961	--	15	--
Consolidated Edison	Babcock & Wilcox	Peekskill, N. Y.	500	140 ^d	1960	100	--	8
Consumers Public Power	Atomics Int., NAA	Hallam, Neb.	240	75	1960	--	25	--
Florida Power Combine	Babcock & Wilcox	Tampa, Fla.	~ 500	200	1962	?	--	?
Middle South Utilities	?	?	~ 80	20	?	?	?	--
New England Electric	?	?	~ 600	200	1963	?	?	--

^b As 27% U²³⁵

^c With Nuclear Power Group

^d Additional 96 Mw electricity from oil-fired superheater

<u>Reactor</u>	<u>Designer</u>	<u>Location</u>	<u>Heat (Mw)</u>	<u>Electric (Mw)</u>	<u>Comple- tion Date</u>	<u>Estimated Annual Processing</u>		
						<u>(kg U²³⁵)</u>	<u>(metric tons U)</u>	<u>(metric tons Th)</u>
<u>POWER DEMONSTRATION REACTOR PROPOSALS, continued</u>								
PAR	Westinghouse	Pennsylvania	580	150	1962	--	--	12
Pacific Gas & Elec.	General Electric	Pleasanton, Cal.	12	3	1957	20	--	--
Rural Coop. Power Assoc.	AMF Atomics	Elk River, Minn.	58	18 ^e	1960	8	2	--
Wolverine Electric	Foster Wheeler	Hersey, Mich.	24	6 ^e	1959	2	--	--
Yankee Atomic	Westinghouse	Rowe, Mass.	480	134	1960	--	22	--
(Liberty Ship)	?	?	~ 50	--	?	?	?	--
(Merchant Ship)	Babcock & Wilcox	?	~ 60	-	1959	?	?	--
			<u>(4350)</u>	<u>(1293)</u>		<u>(1690)</u>	<u>(108)</u>	<u>(20)</u>

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RESEARCH REACTORS

Alabama Polytech. Inst.	?	Auburn, Ala.	?	--	?	?	--	--
Armour Research Inst.	Atomics Int., NAA	Chicago, Ill.	0.05	--	1956	--	--	--
Battelle Memorial Inst.	AMF Atomics	Columbus, Ohio	1	--	1956	0.3	--	--
Brookhaven Research	Brookhaven	Upton, N. Y.	30	--	1950	?	?	--
Brookhaven Medical	Nuclear Dev. Corp.	Upton, N. Y.	1	--	1958	1	--	--
Case Inst. of Tech.	?	Cleveland, Ohio	10	--	1959	8	--	--

^e Additional 4 Mw electricity from hydrocarbon-fired superheater

Reactor	Designer	Location	Heat (Mw)	Electric (Mw)	Comple- tion Date	Estimated Annual Processing		
						(kg U ²³⁵)	(metric tons U)	(metric tons Th)
RESEARCH REACTORS, continued								
CP-5	Argonne	Lemont, Ill.	2	--	1954	1	--	--
Curtiss-Wright	Daystrom	Quehanna, Pa.	1	--	1957	1	--	--
Dow	?	Midland, Mich.	~ 5	?	1960	?	--	?
Ft. Belvoir	Walter Kidde	Ft. Belvoir, Va.	~ 60	20	?	?	--	--
Gamma Corp.	?	Mansfield, Mass.	0.1	--	1957	--	--	--
General Dynamics	Convair	San Diego, Cal.	1	--	1957	1	--	--
Georgia Inst. of Tech.	?	Atlanta, Ga.	?	--	?	?	--	--
Ind. Reactor Labs.	AMF Atomics	Plainsboro, N. J.	5	--	1957	4	--	--
LITR	ORNL	Oak Ridge, Tenn.	3	--	1950	2	--	--
Lovelace Foundation	Convair	Albuquerque, N. M.	1	--	?	1	--	--
LPTR	Foster Wheeler	Livermore, Cal.	1	--	1957	1	--	--
MIT	ACF Industries	Cambridge, Mass.	1	--	1957	1	--	--
Naval Research Lab.	N.R.L.	Washington, D. C.	0.1	--	1956	--	--	--
N. Carolina State	N. C. State	Raleigh, N. C.	0.02	--	1953	--	--	--
NRX	AECL	Chalk River, Canada	40	--	1947	--	~ 10	?
Omega West	Los Alamos	Los Alamos, N. M.	2	--	1956	2	--	--
ORNL Graphite	ORNL	Oak Ridge, Tenn.	4	--	1943	?	?	--
ORR	ORNL	Oak Ridge, Tenn.	20	--	1957	15	--	--
Pennsylvania State	Penn. State U.	University Park, Pa.	1	--	1955	1	--	--

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Reactor	Designer	Location	Heat (Mw)	Electric (Mw)	Comple- tion Date	Estimated Annual Processing		
						(kg U ²³⁵)	(metric tons U)	(metric tons Th)
RESEARCH REACTORS, continued								
Rhode Island University	?	Kingston, R. I.	?	--	?	?	--	--
Stanford Research Inst.	?	Menlo Park, Cal.	10	--	1957	10	--	--
Union Carbide	AMF Atomics	Tuxedo Park, N. Y.	5	--	?	4	--	--
U. of Buffalo	AMF Atomics	Buffalo, N. Y.	1	--	1957	1	--	--
U. of California	Atomics Int., NAA	Los Angeles, Cal.	0.05	--	1956	--	--	--
U. of Miami	Prosperity	Coral Gables, Fla.	?	--	?	?	--	--
U. of Michigan	Babcock & Wilcox	Ann Arbor, Mich.	1	--	1956	1	--	--
U. of Utah	?	Salt Lake City, Utah	?	--	?	?	--	--
U. of Virginia	?	Charlottesville, Va.	?	--	?	?	--	--
U. of Washington	?	Seattle, Wash.	~ 20	5	?	?	?	--
Vanderbilt University	?	Nashville, Tenn.	?	--	?	?	--	--
Washington State College	General Electric	Pullman, Wash.	0.1	--	?	--	--	--
Water Boiler	Los Alamos	Los Alamos, N. M.	0.04	--	1944	--	--	--
Watertown Arsenal	Bendix	Boston, Mass.	1	--	1958	1	--	--
			(227)	(25)		(56)	(10)	(0)

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<u>Reactor</u>	<u>Designer</u>	<u>Location</u>	<u>Heat (Mw)</u>	<u>Electric (Mw)</u>	<u>Comple- tion Date</u>	<u>Estimated Annual Processing</u> (kg U ²³⁵)	<u>(metric tons U)</u>	<u>(metric tons Th)</u>
<u>MILITARY REACTORS</u>								
ALPR	Argonne	Arco, Idaho	3	0.2	1958	3	--	--
APPR-1	Alco Products	Ft. Belvoir, Va.	10	2	1957	6	--	--
APPR-1a	?	Alaska			?	4	--	--
 FIR	 Amer. Rad. & Std.	 Lathrop, Cal.	 ~ 20	 --	 1958	 15	 --	 --

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<u>Designer</u>	<u>Location</u>	<u>Heat (Mw)</u>	<u>Electric (Mw)</u>	<u>Comple- tion Date</u>	<u>Estimated Annual Processing</u>	<u>(kg U²³⁵)</u>	<u>(metric tons U)</u>	<u>(metric tons Th)</u>
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TESTING REACTORS

Bulk Shielding	ORNL	Oak Ridge, Tenn.	0.1	--	1950	--	--	--
ETR	General Electric	Arco, Idaho	175	--	1957	160	--	--

<u>Reactor</u>	<u>Designer</u>	<u>Location</u>	<u>Heat (Mw)</u>	<u>Electric (Mw)</u>	<u>Comple- tion Date</u>	<u>Estimated Annual Processing</u> <u>(kg U²³⁵)</u>	<u>(metric tons U)</u>	<u>(metric tons Th)</u>
<u>TESTING REACTORS, continued</u>								
MTR	ORNL	Arco, Idaho	40	--	1952	30	--	--
Shield Mockup	ORNL	Oak Ridge, Tenn.	?	--	1958	?	--	--
Shield Test	?	Arco, Idaho	?	--	?	?	--	--
Tower Shielding	ORNL	Oak Ridge, Tenn.	0.1	--	1954	--	--	--
			(476)	(0)		(271)	(0)	(0)
<u>PRODUCTION PROGRAMS</u>								
Hanford (B,C,D,DR,F,H, KE,K')	General Electric	Richland, Wash.		--	1944			
Savannah River (R,P,K, L,J)	DuPont	Aiken, S. C.		--	1954			
SCRUP (NRU)	AECL	Chalk River, Canada		--		--	--	--
				(0)		(0)	(0)	(0)

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<u>Reactor</u>	<u>Designer</u>	<u>Location</u>	<u>Heat (Mw)</u>	<u>Electric (Mw)</u>	<u>Comple- tion Date</u>	<u>Estimated Annual Processing</u> (kg U ²³⁵) (metric tons U)	<u>(metric tons Th)</u>
<u>EXPORT</u>							
Argentina	General Electric	Buenos Aires	3	--	?	2	--
Australia	?	-	?	?	?	?	--
Austria	?	-	~ 40	10	?	?	--
Belgium	ACF Industries	-	?	--	?	?	--
Belgium	Westinghouse	-	43	11.5	1958	--	2
Belgium	Nuclear Dev. Corp.	Mol	?	--	1958	?	?
Belgium	Nuclear Dev. Corp.	-	?	--	1959	?	?
Brazil	Babcock & Wilcox	Sao Paulo	5	--	?	4	--
Brazil	ACF Industries	-	?	--	?	?	--
Canada	AEI Atomics	Hamilton	?	--	1958	?	?
Ceylon	?	-	?	--	?	?	?
Chile	?	-	?	--	?	?	?
Colombia	?	-	?	--	?	?	?
Colombo Plan	?	Manila, P. I.	?	--	?	?	?
Costa Rica	?	-	?	--	?	?	?
Denmark	Atomics Int., NAA	-	5	--	1957	4	--
Denmark	Foster Wheeler	Roskilde	5	--	1957	4	--
Dominican Republic	Glenn L. Martin	Ciudad Trujillo	59	12.5	1959	--	?
Ecuador	?	-	?	--	?	?	?

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Reactor	Designer	Location	Heat (Mw)	Electric (Mw)	Comple- tion Date	Estimated Annual Processing		
						(kg U ²³⁵)	(metric tons U)	(metric tons Th)
EXPORT, continued								
Fiat	Westinghouse	-	40	10	?	?	2	--
France	?	-	?	--	?	?	?	--
Germany	?	-	10	--	?	?	?	--
Germany	Babcock & Wilcox	Hamburg Shipbuilding	1	--	1957	1	--	--
Germany	Babcock & Wilcox	-	25	?	?	?	?	--
Germany	Babcock & Wilcox	-	50	?	?	?	?	--
Germany	?	Rhein.-Westphal. E.	40	10	?	?	?	--
Germany	AMF Atomics	University of Munich	1	--	1957	1	--	--
Germany	Atomics Int., NAA	Frank.U.-Darms. U.	0.05	--	1957	--	--	--
Germany	Atomics Int., NAA	City of W. Berlin	0.05	--	?	--	--	--
Greece	?	-	0.3	--	?	--	--	--
Guatemala	?	-	?	--	?	?	?	--
Haiti	?	-	?	--	?	?	?	--
India	?	-	?	?	?	?	?	--
Ireland	?	-	?	--	?	?	?	--
Israel	?	-	10	--	?	8	--	--
Israel	AMF Atomics	-	1	--	?	1	--	--

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Reactor	Designer	Location	Heat (Mw)	Electric (Mw)	Comple- tion Date	Estimated Annual Processing		
						(kg U ²³⁵)	(metric tons U)	(metric tons Th)
EXPORT, continued								
Italy	ACF Industries	CNRN, Ispra	5	--	1958	4	--	--
Italy	Westinghouse	-	~ 20	5	?	?	?	--
Italy	Westinghouse	-	480	134	?	--	22	--
Italy	?	-	~ 500	~ 150	?	?	?	--
Japan	Atomics Int., NAA	Tokyo	0.05	--	1957	--	--	--
Japan (2)	?	-	2 ^j	--	?	?	?	--
Japan	AMF Atomics	-	10	--	?	?	?	--
Latin America ^k	Atomics Int., NAA		~ 40	10	?	?	?	--
	General Electric	-	~ 40	10	?	--	?	--
	General Electric		~ 40	10	?	--	?	--
Lebanon	?	-	?	--	?	?	?	--
Netherlands	ACF Industries	-	20	--	1959	15	--	--
Netherlands	AMF Atomics	Amsterdam	1	--	1957	1	--	--
New Zealand	?	-	?	--	?	?	?	--
Norway	?	-	?	?	?	?	?	--
NPD (Canada)	General Electric	Des Joachims, Ont.	86	20	1959	--	?	--
Pakistan	?	-	?	--	?	?	?	--
Peru	?	-	?	--	?	?	?	--
Philippine Islands	?	Manila	~ 240	60	?	--	?	--
Portugal	?	Lisbon	1	--	1958	1	--	--

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^j 2 reactors at 1 Mw each

^k Probably to be delivered to Brazil, Cuba, and Mexico

<u>Reactor</u>	<u>Designer</u>	<u>Location</u>	<u>Heat (Mw)</u>	<u>Electric (Mw)</u>	<u>Comple- tion Date</u>	<u>Estimated Annual Processing</u>	<u>(metric</u>	<u>(metric</u>
						<u>(kg U²³⁵)</u>	<u>tons U)</u>	<u>tons Th)</u>
<u>EXPORT, continued</u>								
Puerto Rico	?	-	~ 80	20	?	?	?	--
Spain	General Electric	Moncloa	3	--	1957	2	--	--
Spain	General Electric	-	40	10	?	?	?	--
Sweden	?	-	?	?	1959	?	?	--
Sweden	ACF Industries	-	30	--	1958	?	?	--
Switzerland	?	-	?	?	?	?	?	--
Switzerland	ORNL	Wureulingen	1	--	1955	1	--	--
Thailand	?	-	?	--	?	?	?	--
Union of S. Africa	?	-	?	--	?	?	?	--
Uruguay	?	-	?	--	?	?	?	--
Venezuela	?	-	1	--	?	?	?	--
Venezuela	General Electric	Caracas	3	--	?	2	--	--
Venezuela	?	-	5	--	1958	?	?	--
Yugoslavia	?	-	?	--	?	?	?	--
			<u>(1986)</u>	<u>(483)</u>		<u>(51)</u>	<u>(26)</u>	<u>(0)</u>

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