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**Proceedings of the
AEC Symposium for**

Chemical Processing of Irradiated Fuels

**from Power, Test, and Research
Reactors**

**Richland, Washington
October 20 and 21, 1959**

Subject Category: CHEMISTRY—SEPARATION
PROCESSES FOR PLUTONIUM AND URANIUM

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Issuance Date: January 1960

Division of Production
United States Atomic Energy Commission

1
2
3

4
5
6

7
8
9

CONTENTS

INTRODUCTION

Welcoming Remarks	J. E. Travis	1
Welcoming Remarks	W. E. Johnson	3
Objectives of the AEC Power Fuel Processing Program	G. F. Quinn	5
Scope of the Power Fuel Processing Program	F. P. Baranowski	10

HANFORD SESSION

Management Considerations Relative to Hanford	V. R. Cooper	17
Receiving, Storage, and Mechanical Operations at Hanford for Chemical Processing of Power Reactor Fuels	L. L. Zahn, Jr.	26
Chemical Processing of Power Reactor Fuels by the Hanford Atomic Products Operation	A. M. Platt	41
Measurements	K. M. Harman and R. A. Schneider	56

IDAHO SESSION

ICPP Plans for Processing Irradiated Fuels from Research, Test, and Power Reactors	C. E. Stevenson	86
ICPP Facilities for Receiving, Storage, and Mechanical Treatment	A. L. Ayers and C. B. Leek	99
ICPP Dissolution, Extraction, and Waste Treatment Processes and Facilities	F. M. Warzel	113
ICPP Input Measurement Program	F. H. Tingey	144

TUESDAY NIGHT MEETING

The United Kingdom Civil Power Processing Programme	T. Tuohy	158
Eurochemic, Its History and Program	E. Detilleux	167

SAVANNAH RIVER SESSION

Processing Power Fuels at the Savannah River Plant	H. L. Hull	172
Mechanical Handling of Chalk River and PRDC Fuel	J. W. Langhaar	174

Chemical Processing of Chalk River Fuels	H. L. Hull	187 ✓
Chemical Processing of PRDC Core Fuel.	H. L. Hull	195 ✓

OAK RIDGE SESSION

Fuel Processing Facilities at ORNL.	H. E. Goeller	206 ✓
Chemical Processing of Power and Research Reactor Fuels at Oak Ridge National Laboratory	R. E. Blanco et al.	234 ✓
Mechanical Processing of Spent Power Reactor Fuel at Oak Ridge National Laboratory	C. D. Watson et al.	307 ✓
Special Problems in Chemical Processing at ORNL	A. R. Irvine	400 ✓
Accountability of Special Nuclear Material at Oak Ridge National Laboratory	W. T. McDuffee	432 ✓
Attendance List		447

WELCOMING REMARKS

by

J. E. Travis, Manager
Hanford Operations Office, U.S.A.E.C.

Good morning, Gentlemen.

It gives me a great deal of pleasure to welcome you on behalf of the Atomic Energy Commission to the Hanford plant, and on behalf of our AEC-sponsored symposium on nuclear fuel processing.

We propose to review for you during the ensuing two days the technology currently available for processing spent fuels from research, test, and power reactors.

As you know, the AEC plans to process, at existing AEC facilities, spent fuels from civilian reactors, until such service is available from private industry.

Now, with this turn-out, and this lively display of interest on the part of industry, it suggests to me that maybe this day isn't too far off.

The problems that the power reactor fuel elements and blanket materials present to the chemical processing field are, in many cases, unprecedented. The chemist will have to tax his ingenuity to the utmost to devise flow sheets to process these materials, which are certainly not designed to make this job easier.

Here at Hanford, where our primary business is the manufacture and separation of plutonium, our operating contractor, the General Electric Company, has been making giant strides in the past decade in pioneering, along with other elements of the Commission's program, the transition from precipitation and batch-type operation, to continuous solvent extraction separation methods.

The challenge of the power reactor fuel element processing problem has been met head-on, and is being solved with the same enthusiasm and dispatch.

I sincerely hope that the program prepared for you the next few

days at Hanford will serve to be informative, and will aid you in your activities in this field, whether you are exploring the possibility of entering the fuels processing field, or are seeking a better understanding of the fuels processing contracts, which some of you are about to enter into with the Commission.

I have one announcement to make before introducing our next speaker.

On Thursday, October 22, for those of you who can stay over, and are interested, we have arranged a bus tour of the plant area. This will include stops at our new plutonium recycle test reactor presently nearing completion, and one of our canyon buildings similar to the one in which we will be processing the spent power fuels.

Details of the tour, and instructions for signing up, are available in the lobby of the theater.

I might add at this point that, after the next speaker, the meeting will officially become, and will be known by the imposing name of, the "AEC Symposium for Chemical Processing of Irradiated Fuels from Power, Test, and Research Reactors", and will be under the chairmanship of Frank P. Baranowski, Chief of the Chemical Processing Branch in Washington AEC's Production Division, the sponsor of this meeting.

I would like, at this time, to introduce Mr. W. E. Johnson, General Electric's General Manager for the Hanford Atomic Products Operation; Mr. Johnson.

WELCOMING REMARKS

by

W. E. Johnson, General Manager
Hanford Atomic Products Operation
General Electric Company

Gentlemen, my function this morning is a pleasant one, and one that I can discharge very quickly, which is to welcome you, on behalf of the General Electric Company, to this city, to this plant, and to this symposium.

For those of you who are visiting here from abroad, you perhaps might like to keep in mind that the atomic energy industry in this country has, from its beginning, or right after the war, been conducted by the government on the basis of the employment of private contractors as operators.

The General Electric Company is such a contractor for this plant. We took it over from the Du Pont Company in 1946. They were the previous contractors, and we have been operating, then, for about thirteen years.

Our General Electric organization is fairly straightforward. We have an Atomic Products Division in the company, which is responsible for the aircraft nuclear propulsion program, also for the Hanford operation, and for the commercial operation at San Jose, known as the Atomic Power Equipment Department.

Hanford, then, is one part of that division, and this organization, in turn, has a number of components. The ones of the most interest to you will be the three product departments, as we call them. One is the Fuels Preparation Department, another one is the Chemical Processing Department, and last, the Irradiation Processing Department. A fourth organization is the Hanford Laboratories.

You will probably learn more about these components during the

next two days.

The plant itself is on an area comprising about six hundred square miles. The plant buildings are dispersed over this area, in order to get the desired amount of isolation, with the reactors being dispersed along the river bank, the chemical processing plant being located, not centrally, but toward the center of this area.

The organization we have here is very strong in technical content, and numbers in total some eight thousand people.

We have been quite interested over the years in observing this battle between those who design fuel elements, and who have as their objective designing and constructing these elements so that they can't, under any circumstances, be corroded away, or anything of this sort, and then the contrary battle on the part of those who want to dissolve them in the separations plants, and these, of course, are conflicting objectives.

We are quite pleased that we have made considerable progress in chemical processing. For example, we have found a way to dissolve zirconium, an important reactor material, in conventional and available equipment.

The General Electric Company is, of course, interested in the development of the private atomic energy business, and I think many of you here are also interested.

The processing of fuels, or reprocessing, is one essential step that must be mastered before we can hand it over to private business. However, many of us do not know when the total scope of the business (the fuel fabrication business, the power business, and the chemical processing business) will be in private hands, but certainly this step has to be taken, and we certainly welcome your participation here today.

OBJECTIVES OF THE AEC POWER FUEL PROCESSING PROGRAM

by

G. F. Quinn, Director
Division of Production
Washington, D. C.

As an introduction to this two-day session at Hanford, I wish to review with you the objectives of the Atomic Energy Commission in the area of processing power fuels and to note the relationship of this meeting to these objectives. Basically, the role of the AEC in the field of irradiated power fuel processing is twofold:

1. In view of the unavailability of chemical processing services as a commercial enterprise, the AEC has agreed to accept irradiated fuels in unprocessed form, and to make financial settlements with reactor operators which provide for the chemical treatment of the irradiated elements to convert the special nuclear material into the standard forms on which credits and fair prices are based (UF_6 for uranium, 235-238 mixtures, metal buttons for plutonium and uranyl nitrate for U-233).
2. In the interest of assisting the establishment of chemical processing as a commercial enterprise as soon as may be feasible, the AEC has conducted a continuing program of research and development on processing methods and has arranged for wide dissemination of technical information as it becomes available.

The program prepared for these two days at Hanford is directed primarily toward the latter, or informational, phase of the AEC program. It is, however, related to the former, which we may call the services phase, in that discussions will include information on the actual methods, handling and processing to be used when fuels from civilian reactors are returned to AEC.

The Federal Register Notice of March 12, 1957, announced the

services that the AEC would offer in providing for the chemical processing of irradiated fuels, and specified the basis upon which charges would be made for such services. In this announcement, the AEC stated that it would be prepared to enter into contracts providing for such services on the basis of the specified charges; the contracts would extend until June 30, 1967. This commitment was conditioned, however, on the nonavailability of commercial processing services. The notice stated that should reasonably-priced private processing services become available, contracts with AEC would be terminated upon no less than 12 months' notice. In this way AEC has served notice that it does not intend to compete with private enterprise in the processing of civilian reactor fuels.

As I am sure you are familiar, the Federal Register Notice specified that charges for these AEC services would be based upon the estimated cost of performing the chemical processing in an assumed multipurpose plant, referred to as the conceptual plant. The technology chosen for the conceptual plant, while it had not been proved out in the laboratories, was specified primarily as a means of identifying those services to be included within the AEC processing charges. At that time AEC had no plans for actually handling the irradiated elements to be returned from civilian reactor operators; we were still optimistic that a privately-owned processing facility would be constructed. Later, when there appeared to be no early prospect for such a commercial enterprise, AEC began planning how to actually handle and treat these materials. These plans are still being developed. The virtue of the conceptual plant, therefore, was that it permitted defining to the reactor operator those services and the charges related thereto which would be an integral part of his over-all economics, even though the processing technology was undeveloped.

How AEC plans to handle these fuels will be discussed in more detail during this two-day meeting. It is important to recognize, however, that the information to be presented at this meeting will not affect the AEC processing charges since these are based on the conceptual plant. Further, it is not the purpose of this meeting to relate the services or the conditions under which AEC will actually process fuel from civilian reactors to those provided in the conceptual plant. Let it suffice to mention that the capabilities to be installed in AEC facilities will be, at the minimum, equal to those services included in the conceptual plant.

As you know, it is AEC's intention to process returned fuels in its existing facilities after making some modest modifications. This intention is based on the objectives of first, recovering the valuable source and special nuclear materials which will be present in irradiated fuels; and second, to develop, on a specific basis, handling and processing techniques for power reactor fuels from which it is hoped information valuable to the establishment of a commercial

processing facility will result. In this meeting the various presentations will cover the modifications to be made to existing AEC facilities for the receipt and processing of irradiated fuels from a number of foreign and domestic licensed reactors. Since existing AEC plants are based on the aqueous method of recovering uranium, thorium and plutonium from irradiated fuels, your attention during these two days will be directed to aqueous processing technology. A great deal of information has been made available on aqueous processing methods at several previous symposia held in the U. S. and abroad. This meeting at Hanford, therefore, is a continuation of our informational program directed toward providing the latest available technical advances in fuels processing. It is our hope that this information will provide a more substantial basis for further studies and evaluations by those interested in the processing of irradiated fuel as a commercial venture. I might mention here, as a preview, that as a further assistance in analyzing the components of self-contained processing facility, the AEC plans to complete by July, 1960, a preliminary plant design incorporating the latest plant proven aqueous processing technology.

At this point I believe it would be appropriate to review the general reasons for the selection by AEC of a plan which will permit actual processing of returned fuels in existing processing facilities at Hanford, Idaho, Oak Ridge and Savannah River rather than the construction of a new multipurpose processing plant. The possibility that some or all irradiated fuels might be accepted by a private processing facility by the middle or late 60's was a major factor in selecting the alternative with the lowest capital investment. Other factors which led to this decision were:

1. The AEC had already established at some of its sites special processing programs which were closely related to the processing of new power fuels. For example, Oak Ridge has over the last several years, been doing considerable work on the thorium process, and Idaho on the highly enriched uranium processes.
2. Solvent extraction capacity within the AEC complex appeared to be adequate to handle the amounts of fuel projected to be received over the next several years.
3. The large variety of different types of fuel required extensive development effort. The use of technical talent at all of the processing installations enabled each site to concentrate on a limited number of fuel types.
4. A change in processing loads for various reasons such as a change in irradiation levels or reactor start-up dates, or even termination of fuel loads from licensed reactors would not seriously affect the level of operation at any one of the sites, since each site considers this source of fuel feed as

an increment to its basic program.

5. The maximum use of existing facilities (solvent extraction, services, etc.) makes it possible to delay start of modification until the latest possible moment, allowing additional time for developing new receiving and dissolving techniques.
6. It is expected that as experience is gained in the handling of fuel elements, many changes in the processes selected may be indicated. A low initial capital investment should make it attractive to improve the processes at a later date.

I hope that the above brief listing of our reasons leading to the selection of the four existing processing facilities for the interim period until private industry can assume this work will assist you in understanding our approach to the assignment of fuel processing responsibilities. More specific comments on fuel assignments at each site will be given in the next talk.

The processing schemes selected at each site in the AEC interim processing program may not be the best ones to use in a privately-owned plant. It is not evident to us at this time what type or size of plant or chemical treatment should be considered as the initial choice for private enterprise. As experience is gained in the receipt and dissolution of the advanced fuels, a great number of the unknowns now present in this field should be eliminated. The close relationship which must exist between the reactor operator and the AEC chemical processor will undoubtedly lead to an exchange of information of value in analyzing the steps to be taken to reduce the cost of the fuel cycle.

In discussing aqueous processing, we initially think of solvent extraction. The meeting today and tomorrow, however, will stress the receiving and dissolving steps of the processing cycle. There are two reasons for this area of emphasis. The development work has been restricted to the use of installed solvent extraction equipment, supporting services and utilities; and these solvent extraction processes for recovery of uranium and plutonium from irradiated fuels have been adequately treated in previous meetings and reports. The extensive work done over the years within the production complex has been concentrated on the more easily dissolved uranium-aluminum type fuels; our processes end with nitrate solutions recovered from the extraction banks. Development work at AEC laboratories has indicated that dissolution methods for the advance fuels could be employed which yield dissolver solutions which can be handled by known extraction technology. These development leads were used as the bases for the investigation of the dissolution processes best suited for coupling with the existing extraction processes.

We are not including in this meeting discussion of the non-aqueous processing schemes. The development contributions of the non-aqueous development program, coupled with the experience accumulated in the aqueous processing program, should provide both the AEC and industry with a firm basis upon which to judge which concepts and assumptions should be used for design of any new chemical processing plant. Development work on the aqueous dissolution processes has already reduced somewhat the concern of the chemical processor toward changes in fuel element composition and in the cladding material.

I wish to emphasize that the information and experience accumulated by the AEC during the interim processing program will be available to industry. We encourage discussions between the AEC chemical processor, the reactor operator and the fuel fabricator on the effects of changes in fuel composition on the processing equipment to be installed by the AEC. Our experience in the AEC production system has emphasized the value of close collaboration between these parties. Civilian power fuel cycles involve at least three different operating organizations for various phases of the fuel cycle, resulting in difficulties in communications. I feel these can be overcome with mutual benefit by extra effort to exchange different points of view. Some of you already know of our interest in establishing, under the processing contract, technical liaison on any proposed changes in the currently planned fuel types. Initial discussions have already taken place between some reactor operators and the AEC on a study to determine the scope of a small processing facility at, or adjacent to, a power reactor site. Initial phases of this study should identify to both parties the requirements for the different types of facilities.

We hope that the AEC plans for processing the various fuels it will be receiving from the reactor operators will stimulate discussion and effort leading to a reduction in the cost of the fuel cycle.

Thank you.

SCOPE OF THE POWER FUEL PROCESSING PROGRAM

by

F. P. Baranowski, Chief
Chemical Processing Branch
Division of Production

In the opening talk by Mr. Quinn, the general scope of the meeting was presented. I would like to make a few additional comments on the scope of this meeting:

Chemical processing, for the purpose of this meeting, will be restricted to the unit operations from the receipt of unruptured irradiated fuels through the preparation of decontaminated nitrate solutions of uranium, thorium and plutonium. The conversion of uranyl nitrate (other than U-233) to UF₆ and plutonium to plutonium buttons will not be covered at this meeting. The presentations will also be restricted to the processing methods to be used by each processing site on its assigned fuels. The irradiated fuels included in the presentations at this meeting are those to be shipped from reactors in operation, under construction and, in one case, a reactor in a very advanced stage of planning. Processing methods and materials of construction chosen for one site may handle fuels assigned to other processing sites. We have not attempted to present an exhaustive treatment of the various combinations of processing methods and fuel types; rather, we are using this meeting to acquaint you with how the AEC is set up, or will be set up, to handle the various fuels it will be receiving from reactor operators. If more information is desired on the use of a head-end treatment selected for one of the assigned fuels on some of the other assigned fuels, it is suggested that you arrange a time for such discussions with the session Chairman concerned. I wish to point out that each site was given specific fuel assignments early in the program. The full potential of each of the head-end schemes is not known. Technical progress on the processing methods included in this meeting will be presented in the various technical journals and meetings as has been the practice in the past. Technical information in the general field of processing irradiated fuels, including non-aqueous methods and also aqueous methods not included in this meeting, is summarized in the AEC quarterly journal, "Reactor Fuel Processing".

The fuel assignments which have already been made to each of

the processing sites are shown in Table I. A number of studies were made on other fuel assignments prior to arriving at the current one. Assignments of other fuels will be made at the appropriate time. The general distribution of fuel types assigned are as follows:

1. All highly enriched fuels are currently planned to be processed at the Idaho plant. No plutonium handling facilities are now available at this site.
2. The major portion of the low enriched fuel load (less than 5% U-235 enrichment) will be processed at Hanford in an arrangement which will not interfere with the basic production program at that site.
3. The thorium type fuels and the foreign 20% enriched uranium-aluminum alloy fuels are assigned to Oak Ridge for processing. Oak Ridge will install equipment which will parallel, to some degree, equipment to be installed at Hanford for stainless steel clad fuels. To use this equipment, as well as for other reasons, such as providing fission product feed to the Fission Product Pilot Plant at Oak Ridge, we have assigned to Oak Ridge some stainless steel clad low enriched fuels for processing. Some of the reactor projects such as EBWR will have small discharges of fuel and can be conveniently handled in the Oak Ridge facility. These assigned fuels, other processing loads, and process development responsibilities should make maximum utilization of the facility.
4. The large intermediate enriched load from the PRDC reactor and the long elements of natural enrichment from the Canadian reactors have been assigned to the Savannah River plant for processing. Savannah River has changed the geometry of its large dissolver to a critical safe one when handling intermediate enriched fuel, by use of inserts in the dissolver. Savannah River has also installed instrumentation in the plant to indicate slight changes in uranium concentrations and thereby maintain U-235 concentration in dilute solutions at a safe level. The assignment of fuels at Savannah River has been made in a way which will not interfere with the basic production program at that site.

The plants at Idaho and Oak Ridge are direct-maintained plants and the plants at Savannah River and Hanford are remote or indirect-maintained plants.

As mentioned in the preceding talk, the discussions will be primarily on the receiving and dissolution steps of the processing cycle. With respect to the receiving step, we have had very little information on the cask shipping procedures proposed for use by the

TABLE I

CURRENT ASSIGNMENT OF FUEL PROCESSING RESPONSIBILITY

REACTOR PROJECTS

<u>IDAHO</u>	<u>HANFORD</u>	<u>OAK RIDGE</u>	<u>SAVANNAH RIVER</u>
PWR CORE	DRESDEN	PRDC BLANKET	PRDC CORE
OMRE	YANKEE	HALLAM	NRU
APPR-1	PWR BLANKET	N. S. SAVANNAH	NRX
VBWR	PATHFINDER	CON. ED.	
RESEARCH AND TEST REACTORS	PIQUA	ELK RIVER	
		RESEARCH REACTORS	
		EBWR	

shippers of irradiated fuels. It was necessary, therefore, to establish cask acceptance criteria for each site using our previous experience in handling irradiated fuel, the installed handling facilities at the sites and our interpretation of the probable methods of handling and shipping highly irradiated fuels. The AEC cask acceptance criteria for each site are now available. The different dissolution systems to be used will be indicated by discussing the fuel types assigned to each site as shown in Table II. The significant dissolution agent is shown after each fuel type. The core of the fuel element is shown before the parenthesis and the cladding is within the parenthesis. The dissolution systems, in some cases, are those which now appear to be most promising to use. Adjustments may be made if new data indicate a substantial advantage and if major commitments on equipment, etc., have not been made.

IDAHO

The Idaho processing systems were installed primarily for process development work. We are making use of these facilities to do the processing work during the interim processing period. Work at Idaho includes sulphuric acid treatment of stainless steel cermet fuels, hydrofluoric acid treatment of uranium-zirconium alloy fuels and nitric acid treatment of uranium-aluminum type fuels in a direct-maintained plant of relatively low capacity. Nitric acid dissolution of uranium-aluminum fuels can be done either in a continuous or a batch dissolver system.

HANFORD

Hanford plans to use Hastelloy-F equipment for sulphuric acid decladding of stainless steel clad fuel, for ammonium fluoride decladding of zirconium clad fuel and for nitric acid treatment of aluminum clad fuels. This material of construction may be the answer for the long sought after dissolver for these three types of fuel cladding. Also included in the Hanford modification program would be a chopper which could be used on some of the fuels.

OAK RIDGE

Oak Ridge facilities, as those at Idaho, have been primarily built for process development work. We are making use of these facilities to process fuels on a routine basis during the interim processing period. The process selected by Oak Ridge can dissolve stainless steel cladding with sulphuric acid and zirconium cladding with ammonium fluoride in ni-o-nel equipment. An alternate process for dissolving stainless steel to be installed at Oak Ridge, under its development program, is

TABLE II

CURRENT ASSIGNMENT OF FUEL PROCESSING RESPONSIBILITY

FUEL TYPES

<u>IDAHO</u>	<u>HANFORD</u>	<u>OAK RIDGE</u>	<u>SAVANNAH RIVER</u>
U-Zr(Zr)-HF	UO ₂ (Zr)-NH ₄ F	U-Mo(SS)-H ₂ SO ₄ *	U-Mo(Zr)-HF
UO ₂ -SS(SS)-H ₂ SO ₄	UO ₂ (SS)-H ₂ SO ₄	UO ₂ (SS)-H ₂ SO ₄ *	U(Al)-HNO ₃
U-Al(Al)-HNO ₃	UO (Al)-HNO ₃	ThO ₂ -UO ₂ (SS)-H ₂ SO ₄ *	
	U(Al)-HNO ₃	U-Al(Al)-HNO ₃	
		U-Zr(Zy)-NH ₄ F	

*Darex Alternate

*Decladding if
sodium bonded

the Darex facility which uses a hydrochloric-nitric acid combination as the dissolving agent to achieve complete dissolution. Also to be included is mechanical decladding equipment for some of the fuels. The Oak Ridge facility is a direct-maintained plant of low capacity. In contrast to only modifying existing facilities, as will be the case at other sites, Oak Ridge will also build a separate head-end treatment unit consisting of two processing cells, an unloading basin and a storage canal.

SAVANNAH RIVER

Savannah River now plans to use a combination of hydrofluoric acid and nitric acid to dissolve PRDC zirconium clad pins and nitric acid to dissolve the Canadian fuels using existing dissolvers of 309 Cb stabilized stainless steel. The PRDC core contains stainless steel bird cages to hold the zirconium pins in a fixed geometry and Savannah River plans to use a removable basket for accumulating undissolved stainless steel pieces.

From the above, it is apparent that the AEC production and development program has dictated, to some degree, the assignment of irradiated fuel. Every attempt was made to assign fuels so as to reduce new capital investment. No firm cost estimates for plant modifications will be presented at this meeting. Engineering work is still proceeding and significant modifications to existing facilities are not expected to begin prior to the first of the coming calendar year.

I would like to identify some important contributions which have been made by the technical personnel at each of the sites following the assignment of specific responsibilities. These definitely are not all of the advances which have been made in the last two years. These contributions are:

1. Preparation of the cask acceptance criteria to be used by the AEC. Those of you having experience in this area recognize the many difficulties which are present in arriving at criteria.
2. The selection of extremely promising materials for use in dissolvers which can contain more than one of the new dissolution agents and can be used for either aluminum, zirconium or stainless steel clad fuels.
3. The development of control instrumentation to measure slight increases in U-235 quantities in dilute solutions.
4. The technique for making dissolvers geometrically safe from a criticality viewpoint by using inserts.

5. The technique of using baskets to remove undissolved material from dissolvers.
6. The development of techniques and the design of a dissolver to allow examination of dissolver contents after dissolution, if such examination is required.
7. The development of a method to de-jacket some fuel types and a method to chop elements exposing core material to leaching by the conventional dissolution methods.
8. The actual processing of uranium-zirconium alloys and UO_2 stainless steel cermet fuels.

An important function of the processing program is the measurement of the source and special nuclear material recoverable from irradiated fuel. The dollar value of the recoverable source and special nuclear material to be transferred from the reactor operator to the AEC chemical processor is high. The power fuel processing program introduces new measurement problems at the dissolution stage of the process. The need to obtain a good measurement of the source and special nuclear material content does play an important part in the selection of the processing scheme to be used by a chemical processor. For these reasons, each site will comment on the chemical plant measurement system for source and special nuclear material contained in irradiated fuels.

In conclusion, we feel that significant progress has already been made in the development of reasonable head-end processing schemes for a number of the advanced types of fuel elements. The experience which will be accumulated from using the varied chemical and mechanical technologies at the four sites should remove many of the unknowns and uncertainties currently of concern to a chemical processor. It is our feeling that the chemical process development work can keep up with changes to more advanced fuel types which may be more difficult to process than those referred to in this meeting. However, the development and the related capital changes, for handling the new fuel types, can be greatly simplified if the close working arrangement between the fuel fabricator, reactor operator, and AEC chemical processor, mentioned by Mr. Quinn, can be realized.

MANAGEMENT CONSIDERATIONS RELATIVE TO HANFORD

By V. R. Cooper

Chemical Processing Department
Hanford Atomic Products Operation
General Electric Company
Richland, Washington

ABSTRACT

A plan for Hanford Works participation in the Atomic Energy Commission's interim chemical processing arrangement for power, test and research reactor fuels, has been designed. It follows five principal guidelines or considerations. From these considerations it was determined that a scheme utilizing a currently retired obsolete wartime facility could be modified and employed for the receiving, storage and feed preparation operations. The currently operating Redox plant can be incorporated into the plan to accomplish the decontamination and separation of uranium and plutonium for return to the nuclear materials cycle. The resultant system can accommodate uranium and plutonium bearing fuels enriched to a maximum of five percent U-235 or equivalent composed of metallic or ceramic cores; clad with Zircaloy, stainless steel or aluminum. The manifold direct and supporting functions can be provided with minor exceptions from the present Hanford organization. The facilities will be ready to receive fuels in January 1961 and to begin chemical processing one year later. Actual processing schedules will be developed around a campaign basis to yield maximum utilization of processing facilities and minimum isotopic degradation of the recovered uranium. Engineering cost information will be obtained during the course of the program to provide industry with some of the information needed for appraising the possibilities of a private capital venture. The assignment of responsibilities regarding processing, engineering and operation are briefly considered.

* * * *

GUIDELINES - In harmony with the general principles and considerations that have been outlined by Mr. Baranowski, the chemical processing function at Hanford has been planned and carried forward within the following guidelines:

1. Minimum New Capital Investment.

2. Capability to Accommodate fuels enriched to 5 percent U-235 or equivalent.
3. Provide accurate measurements of the fissionable material content in each fuel shipment.
4. Advance the technology as appropriate and consistent with the other limitations.
5. No interruption to the primary Hanford mission of producing weapons grade plutonium.

MATERIAL TO BE PROCESSED - Table I is an abbreviated description of the fuels that are now assigned to Hanford.

The first column designates the reactor by name, operator and designer.

The second column indicates the probable time of discharge. These dates provide the basis for setting the target dates for completing construction work at Hanford.

The third column shows the initial U-235 enrichment as well as the expected discharge concentration. Inspection shows considerable leeway to exist between the allowable concentration of 5 percent and those scheduled for assigned fuels.

The fourth column shows that all generally accepted cladding materials will be represented. Also that UO_2 is the dominant core material. The only exception being the U-Mo core for the Piqua reactor.

The last column lists the dimensional characteristics of the fuel assemblies. The range of lengths indicated can be readily accommodated in the currently existing designed and conceived equipment although some mechanical operations will be necessary on the Yankee fuel before it can be charged to the dissolver.

In addition to the reactors shown, it is anticipated that Hanford will have the capability to process fuels from other power reactors with later construction starting date; such as, PC&E - Humboldt Bay station, Nuclear Power Associates - Carolina-Virginia station and Consumers Power Co. - Big Rock Point station. The only test reactor thus far scheduled is the Plutonium Recycle Test Reactor.

FACILITIES TO BE USED - The processing program at Hanford will utilize three existing plants. They are: (1) The 221-U building which was originally built for the wartime bismuth phosphate process, (2) the Redox plant, the first large-scale solvent-type fuel processing plant built in this country, and (3) the Uranium Calcination plant for converting uranyl nitrate solutions to uranyl oxide powders. This symposium is confined to those operations leading to the separation of decontaminated uranium and plutonium nitrate solutions. Accordingly,

TABLE I
FUELS SCHEDULED FOR HANFORD

<u>REACTOR</u>	<u>FIRST DISCHARGE</u>	<u>% FUEL ENRICHMENT</u>	<u>TYPE OF MATERIAL</u>	<u>FUEL ASSEMBLY DIMENSIONS</u>
	<u>BY CALENDAR YR.</u>	<u>INITIAL (TO SPENT)</u>	<u>CLADDING CORE</u>	<u>CROSS-SECTION, LENGTH, INCHES</u>
DRESDEN COMMONWEALTH - EDISON GENERAL ELECTRIC	3rd QUARTER 1960	1.5 0.7	Zr-2 UO ₂	4.4 SQ. x 134.2
YANKEE YANKEE ATOMIC ELECTRIC WESTINGHOUSE	4th QUARTER 1961	3.4 2.63	348-SS UO ₂	7.62 SQ. x 111.2
PATHFINDER NORTHERN STATES POWER ALLIS CHALMERS	1st QUARTER 1963	1.8 0.77	800I-AI UO ₂	5.14 SQ. x 96.4
OMR (PIQUA) AEC ATOMICS INTERNATIONAL	3rd QUARTER 1962	ca2. ca1.4	2S AI U-3.5Mo 0.2AI	5.12 DIA. x 86
PWR (SHIPPINGPORT) AEC AND DUQUESNE POWER AND LIGHT WESTINGHOUSE	1964	NATURAL	Zr-2 UO ₂	5.6 SQ. x 110

the conversion operation, although a part of the project, will not be included in the series of more detailed papers describing the status of the Hanford program.

Figure I (Area Plan) illustrates the location of these facilities within the Hanford reservation. Transportation of incoming and outgoing materials from these facilities can be accomplished by truck and rail facilities connecting from the Hanford area to four major railway systems and the national highway network. Barge shipment via the Columbia river to the Port is also a possibility. However, transshipment into the Hanford Works via rail or truck will be the responsibility of the shipper.

BASIS FOR USE OF REDOX VERSUS PUREX - The decision to employ the Redox plant, rather than the more recently built Purex plant, was made on the basis of distributing the chemical processing functions in that manner which would maximize the production capabilities of our existing separations plants. This point is made to arrest any implications that a breakthrough in the Redox hexone process has been made which overtakes the technical, engineering and economic advantages attributed to the Purex-type processing scheme that has been employed in the more recently built facilities at Hanford, as well as Savannah River.

BASIS FOR SYSTEM COMPONENTS - The facilities to be used and the basic material flow scheme are shown on (Figure II - NPF Material Flow Scheme). With the exception of the cask transfer building and the pipeline connecting the U plant and the Redox plant the buildings and waste tanks shown are now in place. The principal question to be resolved in arriving at this arrangement was the inclusion of the U plant versus modifications within the Redox plant plus new structures. Two factors dictated the use of U plant. The necessity for a campaign basis of operation and possible future changes in the fuel preparation system. A campaign system of operation is essential if costly degradation by mixing uranium of differing isotopic compositions is to be avoided. There are also justifications for segregating the plutonium although they are not as readily tied to a dollar figure. This campaign approach requires storage facilities for fuel assemblies as well as storage of dissolved fuels since chemical processing may occur as infrequently as every six months. This follows from the considerably larger capacity of the Redox plant than the load represented by power, test and research reactors.

Although it is believed that currently specified fuel claddings and cores can be processed in the planned dissolver system, it is entirely possible that future changes in fuels could alter this situation. The desirability for space to accommodate new equipment is readily recognized although the extent of justification is nebulous.

The latent adaptability of the U plant, primarily spare cells, was in sharp contrast to the very specific and limited capability offered by the altered Redox plant supplemented with new facilities. Furthermore, modifications within the Redox plant and nearby area were estimated to cause an operating interruption of 6 to 12 months.

Figure 1

Figure 2

BASIS FOR NEW DISSOLVER SYSTEM - The initial dissolution procedure will use chemical dejacketing of the fuels. This approach minimizes the possibilities for the diversion of unknown quantities of fissionable material that is inherent in the simpler dissolver system based on nitric acid leaching of segmented fuels. The dissolver system must accordingly be capable of withstanding attack by each of five chemical mixtures - three different mixtures for the three different cladding materials - two different mixtures for the two different core materials. The resulting pair of solutions - dissolved jacket and dissolved core - can be analyzed for fissionable material. The assay plus volumetric measurements will provide information on the total quantity of fissionable material in the fuel charged to the dissolver.

Provisions will be made in the mechanical processing cell to segment fuels. If certified measurements can be provided as to the amount and isotopic composition of uranium in the virgin fuel elements it should be possible to arrive at a satisfactory settlement of the source and fissionable material contained from analysis of the solution resulting from acid leaching of segmented fuels. The details concerning this are discussed in the paper "Measurements" by K. M. Harmon and R. A. Schneider.

The dissolver system under either mode of operation is the capacity limiting operation. Based on the projected quantity of fuel to be processed until 1967, as shown on (Figure III - Estimated Receipts), a single dissolver unit will have adequate capacity to satisfy the scheduled fuel processing load despite the charging limitations imposed by critical mass considerations. As evident from the chart, the maximum throughputs of 71 tons of uranium are reached in 1964, 1966 and 1967.

IMPACT ON HANFORD ORGANIZATION - Exclusive of construction activity, the impact of the power fuels chemical processing activity on the Hanford operation has been principally a matter of rearrangement and rescheduling of research, development and engineering activities. The principal characteristics found in the power fuels as compared to the present Hanford production fuels were foreseen to be applicable to the future Hanford fuels for plutonium production. Consequently some studies were in progress or programmed in the chemical processing field that were readily meshed with the technology required for power fuels processing. Acceleration of development and engineering work as required by the power fuels program has required the stretch-out or deferment of some study areas associated with processing of present fuels.

The presence at Hanford of other R&D programs as well as functional services has provided support in terms of facilities, personnel and knowledge that have been and will be effective in establishing and operating the facility. For example, the critical mass physics activity has been an important factor in approaching the equipment design and spacial arrangement as well as operational considerations on a sound basis. With the completion of the critical mass laboratory now under construction we anticipate further gains in

U IN METRIC TONS; Pu IN KILOGRAMS

ESTIMATED RECEIPTS URANIUM AND PLUTONIUM BY CALENDAR YEAR

Figure 3

knowledge that will permit innovations in design and operation to be evaluated on the basis of tests on prototypical equipment rather than idealized mathematical models. From this knowledge further advances in equipment design parameters and operational limits are expected that ultimately will bring about reductions in capital and operating costs.

The effect of the program on the organizational components responsible for operating and supporting functions is forecasted to be minor. Since the processing is campaigned, the staffing for the fuel receiving, storage and dissolution functions can to a large extent be made by rotating personnel assigned like-functions to and from the Redox plant area. There will be some functions to perform relating to building operations, maintenance, fuel handling and mechanical processing, that will require added personnel. Overall, this is not expected to exceed 9 to 15 persons.

The new analytical chemistry functions are primarily associated with accountability measurements rather than process. Since they are not critical time-wise, they can be absorbed reasonably without adding personnel.

The more generalized supporting functions represented by shops, stores, radiation monitoring protection, are believed adequate in terms of facilities and personnel to absorb the new activity without change.

COST CONSIDERATIONS - It is believed that any high spot statements of the estimated construction costs associated with the individual phases of the project would prove confusing; unless, bases for distributing indirect costs, extent of costs associated with functions beyond the production of uranyl and plutonium nitrate solutions and similar matters were examined at more length than this discussion permits.

As indicated by Mr. Baranowski in his presentation, the cost of processing will be based upon stipulations stemming from a conceptual plant design. Engineering-type cost information and performance information will be collected and correlated to permit better costs to be assigned to operational steps such as mechanical processing, dissolution, chemical separation and waste disposal that will be of interest to industry in gauging the possibilities for a free enterprise business. Detailed cost accounting will be performed whenever special circumstances to be defined within the processing contract necessitate such information.

SCHEDULE CONSIDERATIONS - The schedule for completing the facilities is divided into two phases. We anticipate completion of the facilities for receiving and storage of fuel elements by January of 1961. This coincides closely with the anticipated receipt of this first fuel discharge from the Dresden reactor. The processing system will be completed one year later in January of 1962. This later target was established on the basis of bringing the project to a timely conclusion consistent with the delivery of specialized

engineered equipment, returning the material into the fuel cycle at a reasonable date and gaining operating experience in advance of the receipt of fuels from all assigned reactors.

The schedule for chemical processing of fuels from the several reactors will be dependent upon two considerations. First, the fuel must be cooled until the short-lived highly radioactive U-237 has decayed to a low level. Obviously this isotope would accompany the product uranium and prohibit operation of the unshielded system for conversion of uranyl nitrate to uranium trioxide. This is established at two parts U-237 to 200 billion parts of U-238. A maximum of about 150 days cooling is estimated. Second, and probably overriding is the requirement that the fuels be processed in a sequence that will afford maximum utilization of the processing facilities and also result in the lowest incremental operating cost.

RESPECTIVE RESPONSIBILITIES - Responsibilities associated with the program are divided as follows: Technical, engineering and operating aspects are assigned to the Hanford Atomic Products Operation of the General Electric Company. The Chemical Processing Department has been designated to manage these phases of the program. As indicated by Mr. Baranowski, the contractual relationships with the reactor operators are the responsibility of the Hanford Operations Office of the Atomic Energy Commission. Detailed design of the receiving, storage, mechanical processing and dissolution facilities, as well as some assistance in scope engineering, will be performed by the Vitro Engineering Company under contract to the Hanford Operations Office.

RECEIVING, STORAGE, AND MECHANICAL TREATMENT OPERATIONS AT HANFORD
FOR
CHEMICAL PROCESSING OF POWER REACTOR FUELS

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ABSTRACT

Plans at Hanford for its cask receiving and unloading, fuel element storage, and mechanical processing functions under the Non-Production Fuels Processing Program are outlined in this paper. These operations will be performed, along with dissolution and metal solution storage, in Hanford's 221-U Building built originally for the now-obsolete bismuth-phosphate separations process. The one new building planned for Hanford under this program will house a crane to transfer the shipping cask to a Hanford railcar for admittance to the 221-U Building, thereby protecting the cross-country car or truck from accidental contamination. The cask unloading and fuel element storage provisions within the 221-U Building are described in the paper. Mechanical equipment is planned to complement Hanford's fundamental approach to decladding of fuel elements by chemical means in geometrically safe equipment. The functions of the mechanical cell will include sawing of end fittings, shearing through core material containing sections, examination of dissolver debris following chemical dissolution, and special operations such as separating the Yankee fuel element assembly. Hanford's current status under the Non-Production Fuels Processing Program is also described.

* * * *

It was determined that the best assignment of Hanford Non-Production Fuel Processing operations to the 221-U Building area

would be cask receiving and unloading, fuel element storage, mechanical processing of fuel elements, their dissolution, and storage of the metal solution. This paper considers the first three of these operations; namely, cask receiving and handling, metal storage, and mechanical processing. Subsequent steps are the subject of the next paper.

Figure 1 shows the 221-U Building. This building is about 800 feet long, 65 feet wide, and 80 feet high. Approximately half of the building in which the processing operations are performed lies beneath ground level. The auxiliaries that can be noted are the railroad tunnel and the exhaust ventilation system, sand filter, exhaust fans, and stack.

In preparing for the receipt of expended power, test, and research reactor fuel elements at Hanford, many areas of concern somewhat removed from the immediate Hanford problem areas were reviewed. For example, since plans were indefinite with many of the reactor operators regarding their intended form of shipment, it was concluded that Hanford receiving facilities should be suitable for either railroad or truck shipment. In addition, investigations made into details of reactor operator's plans for cask design, independent surveys of cask handling hazards, and analyses of physical limitations of the 221-U Building railroad tunnel led to the development of a Hanford Cask Acceptance Criteria which in turn governed the design of the receiving and handling equipment.

Figure 2 shows the surrounding area of the 221-U Building with the proposed new 213-U Cask Transfer Building shown in relation to it. The Transfer Building will be located approximately sixty feet from the railway tunnel entrance to the 221-U Building. The rail and paved truck access to the Transfer Building can be noted.

Figure 3 shows the 213-U Transfer Building in artists' perspective. The preliminary engineering on the Transfer Building has been completed and detail design is currently in progress. Three main functions will be performed by the Transfer Building. This building derives its name from its primary function, that of transferring the shipping cask from the cross-country railway car or truck to a captive car. The captive car will transfer the cask into the main canyon area via the railway tunnel connecting the Transfer Building and the 221-U Building. This transfer will guard against accidental contamination of the cross-country vehicle by keeping it out of the potentially contaminated canyon area. The Transfer Building will be maintained essentially clean and free from contamination, and all maintenance within it will be performed in a normal contact manner. The second purpose of the Building is to adapt the cask by contact means for the special remote operations, to be described later, that will be performed within the 221-U Building. These operations would include

Fig. 1— The 221-U building.

Fig. 2— Plot plan for transfer station.

installing remote-type nozzles, valves, and other devices essential for the remote crane operations. The third function of the Transfer Building is to provide low-level cask decontamination facilities.

Basically, the Transfer Building will be a simple steel structure for supporting the 75-ton overhead traveling crane. The building will be equipped with a ventilation supply and exhaust system to control temperature and air flow within the building. Floor space will be provided for the storage of casks, and facilities will be available for low-level cask decontamination work. Normal building services will also be provided. Portable scaffolds will facilitate crane maintenance and cask decontamination.

The captive car will be moved into the railroad tunnel by means of the railroad car puller. In this position, the cask will be ready for the operations to be performed prior to opening. It should be emphasized that cask transfer and unloading operations will not be performed simultaneously. In fact, since heavy shielding will not be provided between the Transfer Building and the railroad tunnel, the Transfer Building will normally be evacuated during cask unloading operations.

Before the cask can be unloaded in the Canyon Building safely, several precautions must be observed. It is important to understand that all cask handling and unloading operations at Hanford will be conducted in air, unlike most of the other AEC sites where water basins will be employed. The characteristics of the material being handled, its radioactivity, its rate of energy release, and the hazard of contamination spread must be considered. Cask unloading criteria will be established to serve in describing devices and techniques to be used as a part of the cask unloading procedures. In general, these procedures will be designed to safeguard the canyon building by protecting the fuel element integrity during handling, and by recognizing irregularities before the cask would be opened.

Typical of the control steps to be taken will be the following:

1. Any pressure within the cask will be vented to a closed vent system by remote means. The vent system will adequately decontaminate the off-gas stream before discharge to the main ventilation air stream.
2. The cask interior will be thoroughly flushed to remove any radioactive contamination that may be present. The flushing medium will be monitored to determine presence of any such activity. Abnormal activity levels in the flushing material will indicate the presence of uncontained, ruptured fuel elements within the cask.
3. Where necessary, to prevent thermal shock to fuel elements upon immersion in the water of the storage cell, cooling media will be routed through the cask interior. Depending upon the shipping temperature of the fuel elements, progressive cooling with steam, air and water may be used. The temperature of the fuel elements must be reasonably low in

relation to the storage cell water temperature before the cask would be unloaded and the material transferred to storage.

4. Recognition of a serious abnormality during any of the operations above would delay the unloading of the cask until the necessary contractual and operational resolutions have been made. Unloading of casks under these circumstances would then be done very deliberately and carefully after an acceptable and safe technique has been decided upon.

In order to guard against accidental dropping or breakage of the fuel elements during handling, the Hanford Cask Acceptance Criteria requires that fuel elements be placed within containers by the reactor operator before loading into the cask. This will permit safe handling of the fuel elements within the Canyon Building by the remote crane. For the same reason, Hanford is planning on making all subsequent above-deck fuel element transfers within specially designed containers. Later discussion in this paper will identify two types of such Hanford containers, the storage bucket and the dissolver canister. The storage bucket will contain the integral fuel element assemblies during storage and will be used in making any transfer from storage to the mechanical cell. The dissolver canister will be used in charging the dissolver. Mutual advantages might be developed for the reactor operator and Hanford if the cask containers and the storage buckets were of identical design to facilitate this interchange. This would eliminate one handling operation at Hanford, the transfer of fuel elements from the cask container to the storage bucket. Standardization of containers would permit also more rapid unloading and return of shipping casks and standardization of container handling tools. Normally the empty cask containers would be returned together with the cask to the shipper.

When the cask has been prepared for opening, the lid will be removed remotely, and the remote crane will place the fuel elements within the appropriate storage cell.

Since all transfer operations within the Canyon Building from the point of cask unloading will be performed by the remote crane, a few words of explanation of the technique of remote crane operations may be in order.

Figure 4 shows a typical cross-sectional view of the 221-U Building. The processing area of the building is sub-divided into forty process cells shielded from personnel access areas of the building by thick concrete walls and cover blocks. Above these processing cells is a large canyon area which houses the remote crane needed to service the processing equipment within the cells. This figure shows the crane cab parapet and shielded cab, from which the operator controls the crane. The crane operations are viewed through an optical periscope,

Fig. 3—Cutaway of transfer station.

Fig. 4—The 221 building process ventilation system

which gives the perception needed for operations with the main hook and auxiliaries. The cell cover blocks are removed by the crane when access to the cells is needed. Maintenance of the crane is done by contact means at one end of the canyon building where a platform and maintenance facilities are provided for this purpose.

The figure also describes, in brief, the ventilation provisions of the main canyon building. The flow of air through the building is always maintained in the proper direction so that radioactive contamination cannot progress from contaminated areas into cleaner areas. Air is supplied to the canyon proper by supply units which adequately condition and filter the air before entry. The air then flows under carefully controlled differential pressures into the process cells and pipe tunnel through cracks between the cover blocks and then through ports into the air tunnel. Exhaust fans pull the air from the air tunnel through the exhaust ventilation sand filter and discharge it to the 200 foot high concrete stack. The ventilation system described on Figure 4 is currently in service at the U Plant. However, means of increasing the flow of air in this system are being considered in order that contamination control may be improved consistent with the degree of contamination potential expected for the Non-Production Fuels Reprocessing Program. The sand filter is provided to contain particular activity within the Plant limits and to restrict the release of any such activity to the atmosphere and environs. This filter is capable of removing better than 99 percent of the submicron particles encountered in normal plant operations.

Casks received at Hanford will normally be unloaded within a reasonably short time so that the cask can be returned expeditiously to the shipper. Since subsequent processing operations will be scheduled more at the convenience of Hanford, fuel element storage in the "as-received" condition will be provided.

Figure 5 shows a typical fuel element storage cell as it exists at present, and illustrates one of the advantages of the 221-U Building for these operations. At the present time there are 16 such cells within the U Plant remaining from the previous metal recovery operations there. The large tank shown on the figure is typical of the so-called bathtub tanks planned for fuel element storage. These tanks are 14 feet high, 10 feet in width, and 16 feet in length. The bathtub cells were considered to be adaptable to fuel element storage, since most of the needed services are already in place or rather easily obtained, and since the large bathtub tanks offer the water reservoirs needed for storage and cooling of the fuel elements. The bathtub tanks will be modified by cutting out a portion of the tank and removing the internal pipe coils and fixtures presently installed. Ten of these tanks will be used for fuel element storage.

Fig. 5—Fuel element storage cell.

Preliminary engineering work defining fuel element storage requirements has been completed and detail design work is in progress.

Figure 6 gives a perspective view of the bathtub cell, as modified for the storage function. Several fuel element assemblies are shown in place within the tank. Air lift circulators will be permanently installed within the tank to provide a means for tank content agitation, if needed, for heat transfer, flushing, and tank clean-up for either decontamination or reclamation of fissile material. Trunnion guides will be permanently installed on the top of each tank. The guides will be used to locate equipment to be installed remotely within the tank.

Continued means of safeguarding the fuel element integrity must be employed during storage; the fuel elements must be kept cool; they must be kept in a non-critical array; and they must be protected against accidental damage. The fuel element cooling and nuclear safety functions will be satisfied by storage racks designed specifically to individual reactor requirements. Cooling surface will be provided to maintain the primary coolant temperature below 150°F for the maximum heat evolution case consistent with the storage rack being filled with fuel element containers. Nuclear safety during fuel element storage will be assured by properly baffling the storage rack to maintain a non-critical array of fuel elements in the water-moderated system.

The fuel elements will be cooled by the primary coolant water within the storage tank, which, in turn, will be cooled by a circulating cooling water flow through the coils within the rack. The primary coolant will be monitored carefully to detect the presence of any fission product which would denote a ruptured fuel element. In such a case, the coolant could be routed to concentration equipment for reclamation of any nuclear values. Normally, however, the coolant is left within the tank and is replenished, as necessary, to maintain the normal operating level. Sampling facilities, primary coolant temperature recorders, tank liquid level and specific gravity recorders, and alarms will be provided in connection with the storage tanks to permit proper monitoring of these critical conditions. The secondary cooling water is discharged to a swamp for disposal.

The storage rack will be constructed of a common industrial material such as aluminum, which exhibits corrosion resistance to the water media and boric acid solutions which will be encountered during normal operations only; however, the rack must be removed from the tank before more aggressive reagents could be added in tank decontamination and similar operations. The bathtub tank itself is constructed of stainless steel and will withstand the normal decontamination agents such as nitric acid and caustic which would be used.

Localized ventilation control of the bathtub tanks will not be provided initially. It is expected that the ventilation from the main

canyon ventilation system will control the contamination level of the storage cell adequately. However, vessel vent header connections to the storage cells will be provided and hoods or lids can be installed over the storage tanks, if it is found that a closed vent system is needed to control the spread of particular contamination from within the storage tanks.

Hanford is planning the approach of maximizing chemical operations in preparing the Non-Production Fuels material for solvent extraction processing. However, the dissolving equipment will be made safe by inherent geometry for the richest, most reactive material that can be expected reasonably to be received for processing. In achieving this mode of nuclear safety, mechanical processing of certain fuel elements will be required to permit them to fit within the nuclear safe geometry corresponding to the enrichment level assigned to the total program at Hanford, 5 percent.

Broadly speaking then, the mechanical cell will be provided at Hanford to reduce any fuel elements that may be received to a size suitable for charging to the dissolver system, which will be safe by geometry for 5 percent equivalent enrichment. All equipment within the mechanical cell will be designed to retain critically safe configurations of mechanically processed fuel element components. Preliminary engineering work of a yet-conceptual nature is in progress on the mechanical cell. Complementary development work is being performed within the Hanford Laboratories.

Additional mechanical processing capabilities are also considered warranted in the interest of maintaining efficient power reactor reprocessing capability at Hanford under differing production circumstances. For example, removal of massive end fittings and sub-components could, in many cases, improve reprocessing operations by reducing essential chemical consumptions, waste volumes, or time cycles. Also, dissolver debris will have to be examined in many cases to assure complete dissolution of all fissile and source material. In addition, short-range, high capacity demands upon dissolving equipment may necessitate reduction of fuel elements into the smaller shapes which would permit high density charging of the dissolvers to obtain the accompanying high dissolving rates. From these broad considerations, several functions will be incorporated into the mechanical cell.

Figure 7 is a schematic diagram outlining the broad functional capabilities of the mechanical cell. The functions emphasized here are sawing of massive hardware, shearing of fuel elements through core material containing sections, and examination of dissolver debris. Normally mechanical processing will be maintained at a minimum, and frequently fuel elements will by-pass the mechanical cell completely on their way to the dissolver. However, it is obvious that many other

Figure 6

Fig. 7—Flow diagram.

flow paths through the mechanical cell are available to the Hanford Operation. In many cases dissolver debris will be returned to the mechanical cell for close inspection before disposal. It is anticipated that this debris will be returned occasionally to the dissolver for recovery of any undissolved material of value.

Figure 8 is a perspective of the mechanical cell. This cell arrangement will be fitted into the existing two storage cells just north of the railroad tunnel. The cell will be lined completely with stainless steel plate to reduce the amount of build-up of activity on the floor and wall surfaces and for ease of decontamination. The condition of all of the cells in the 221-U Building at the present time will permit construction operations without undue restriction by radiation levels, once the existing equipment is removed and relatively modest clean-up work is performed. The mechanical cell equipment will be serviced by the remote canyon crane, and material will be conveyed by this mechanism to and from the cell.

Figure 8

All operations in the cell will be observed visually from operating areas through shielding windows strategically located near the critical operating areas. Additional visual inspection can be made using special devices such as mirrors and binoculars. Movement of material within the cell will be accomplished by conveyor mechanisms and the main manipulator system. The manipulator carriage will be cantilevered from tracks on the wall of the cell. The arm and hand of the main manipulator will perform maintenance and special operations. A master-slave manipulator system will be provided also for operations where less strength is required. All manipulator operations will be

controlled from outside the mechanical cell. The manipulators will normally operate above the water level in the mechanical cell.

The water level in the cell will be maintained at a point where the entry cell is sealed from the mechanical cell. All fuel material entering or leaving the cell will pass through this water lock to prevent the escape of contaminated air to the canyon proper. Small equipment and maintenance tools will use the same method of entry to and exit from the mechanical cell. Another lock system will be provided for dissolver buckets moving to and from the shear. This separate system will be provided to keep the water associated with chopped fuel from mixing with the other water in the cell and increasing its level of activity. The canyon remote crane will introduce and remove material from both entry points to the cell; all movements within the cell beyond the point of entry will be performed by self-contained equipment. The maximum length that can be handled in either cell entry is about 15 feet. In the main waterlock, diameters up to about 2 feet can be handled. The shear lock is limited to items of about 8 inches in diameter. Material destined for saw operations in the cell will be brought into the entry water lock within its storage canister. Individual fuel elements will then be removed from the storage bucket by the remote canyon crane and inserted into the cell entry conveyor which will transfer the fuel element from the vertical to the horizontal position while moving it through and under the water lock. A grabber attached to the shoulder of the main manipulator will engage the fuel element and raise it from the cell entry conveyor onto the saw table. The saw will be capable of moving the full length of the saw table on a carriage to make transverse cuts for removal of both end fittings. Special clamps will be provided in conjunction with the saw table to support the fuel element during sawing. If the fuel element assembly with its end fittings removed is scheduled for direct charging to the dissolver from the saw table, the main manipulator will lift it and slide it into the dissolver canister. If the fuel element assembly is scheduled to be sheared, it will be raised by the main manipulator from the saw table to the shear feed conveyor. This conveyor will feed the fuel element assembly into the shear for successive cuts. For shearing operations, the dissolver canister is lowered from the remote crane through the shear access lock. This canister will then catch the shear fragments as they drop from the shear blades. The dissolver canister will be rotated and raised by a tipping device which will cause it to engage the throat of the shear chamber closely to prevent sheared material from dropping into the space around the dissolver canister and creating a nuclear safety hazard. When the dissolver canister catching the shear fragments is filled, it will be tipped back into the vertical position for removal by the main crane. Water-

sprays will rinse the canister as it is raised through the shear lock. The dissolver canister containing shear fragments will be charged either directly in the dissolver or stored in one of the storage tanks until scheduled for dissolution.

Special operations such as those required to reduce the Yankee fuel element assembly into its 9 sub-assembly components will be performed by special tools operated from the main manipulator while the fuel element is on the saw table.

Another function of the mechanical cell will be the examination of dissolver debris before its disposal to assure complete recovery of fissionable material. The dissolver canister will be returned to the cell entry lock from the dissolver following the dissolution step. This canister will be brought into the cell by the entry conveyor system, raised to the level of the examination table and dumped by the main manipulator system. A window in close proximity to the examination table and master-slave manipulator system will permit detailed examination of this debris. In the case of the Piqua fuel element residue which should consist of two concentric stainless steel tubes, transverse sections can be made on the saw table to facilitate inspection on the inspection table. Intermediate operations would be performed by the main manipulator. If the examination table material is determined to be free of fissionable values, the contents will be placed in a burial canister for disposal. If fissionable material is present, the inspection table material would be returned to the dissolver canister for additional dissolving operations. The dissolver canister will be fabricated, of course, from a material which will resist the corrosion of the dissolving solutions involved, perhaps the same material as the dissolver itself. The inspection function of the mechanical cell, initially, will be an important part of the dissolver-mechanical cell operating complex. However, experience will define better the extent of inspection required to assure complete dissolution, and it is anticipated that the inspection operation will become very non-routine, eventually. The mechanical cell will not be designed to perform meticulous types of operations such as precise sampling, examination, or testing of fuel element fragments except as just described.

Primarily, ventilation of the mechanical cell will be accomplished by normal means, as described earlier for the other process cells within the building. The main difference lies in the exhausting of air from the cell. Since it will be impossible to exhaust air from the bottom of the cell, a special exhaust port will be provided from the top of the main mechanical cell area. A small flow of air through the entry cell will be induced by holes through the water seal wall. Problems specific to the mechanical cell, however, require that special

provisions be made for control of excessive amounts of fine material from the sawing and shearing operations. A conventional wet scrubber system will be installed within the cell to filter the cell air and remove particular material which may be present. A large percentage of the fines generated in shearing and sawing operations is expected to enter the water of the mechanical cell. All cutting operations involving the potentially pyrophoric materials, zirconium and metallic uranium, will be done under water.

Water which contains fines from the air scrubbing system, will discharge into the cell water system, which will be filtered in turn. The material recovered on the water filter can be charged either to the dissolver for recovery of fissile material or a disposal canister if no fissile material is present.

Major maintenance work on the mechanical cell equipment will be performed by removing the equipment from the mechanical cell with the remote crane, decontaminating the equipment to permit contact personnel access, and repairing by normal contact means using standard Hanford radiation controls and protective measures. Cell sprays will be provided to effect gross decontamination of the equipment before it is removed from the mechanical cell. Disposal of failed mechanical equipment that cannot be repaired will be by burial. The facilities needed for the major maintenance operations, just described, are essentially in place in the 221-U Building, as it exists today.

The manipulator systems and viewing windows within the mechanical cell will permit minor routine repairs to be made within the cell. Routine change of saw and shear blades will be conducted in this manner by the main manipulator. It may be possible also to do some contact maintenance of mechanical cell equipment from above by removing the cell cover blocks and raising the water level to provide some shielding to personnel working from the canyon deck.

The main manipulator will be removed from the cell for maintenance. It will be designed, however, for ready decontamination by the use of guards and seals to keep activity from entering the working parts. Its exterior surfaces will be of stainless steel to facilitate decontamination. Provisions will be made for washing the manipulator in the mechanical cell before removal.

The next paper will cover the additional processing steps following mechanical treatment. The dissolver canisters, ready for charging to the dissolver, will be stored in one of the fuel element storage cells in preparation for the dissolving operation. These canisters may, upon the circumstances, contain integral fuel elements, simply transferred from the storage buckets to the dissolver canisters; trimmed fuel elements with end fittings removed; or sheared fragments of fuel elements. In all cases, the dissolver canister geometry will conform with that of the geometrically safe dissolver.

CHEMICAL PROCESSING OF POWER REACTOR FUELS

BY THE HANFORD ATOMIC PRODUCTS OPERATION

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ABSTRACT

The chemical processing of low enrichment (less than 5% U_{235}), mechanically processed solid fuels to yield decontaminated and segregated uranium and plutonium products is described. Two step dissolution processes, i.e., cladding removal followed by core dissolution, will be employed in geometrically safe dissolvers. Dissolver effluents will be clarified, stored, and transferred to an existing Redox solvent extraction facility for decontamination and segregation of plutonium and uranium. Existing facilities will also be used for waste disposal.

BACKGROUND

Prior discussion has indicated the significance of chemical processing in Hanford's plans for handling power, research, and test reactor fuels. This discussion will elaborate on those portions of the program wherein the mechanically processed solid fuels will be converted to decontaminated and segregated uranium and plutonium products. It should be noted that our plans for such processing are not nearly as solidified as those of receiving and storage since construction and beneficial occupancy schedules for these facilities lag the others by about one year.

FUEL CHARACTERISTICS

The important chemical and physical properties of the five power reactor fuels presently scheduled for Hanford processing are shown in Figure 1. Two of the fuels have Zircaloy-2 cladding of 27 to 33 mils thickness and contain uranium dioxide cores up to 500 mils in diameter. Two of the fuels are clad in aluminum of 35 to 40 mils thickness and

REACTOR FUELS						
<u>REACTOR</u>	<u>CLAD MATERIALS MILS</u>		<u>CORE MATERIALS MILS</u>		<u>ENRICHMENT % U₂₃₅</u>	<u>TONNES YEAR</u>
DRESDEN	Zy	33	UO ₂	500d	1.5	13
SHIPPING PORT	Zy	27	UO ₂	300d	NAT	13
PATH FINDER	Al	40	UO ₂	340d	1.8	6
PIQUA	Al	35	U-Mo	210†	2.0	4
YANKEE	SS†	21	UO ₂	300d	3.4	<u>24</u> 60

Figure 1

have uranium dioxide or uranium-molybdenum cores up to 340 mils in diameter. The remaining fuel is clad in 21 mils of stainless steel and has a 300 mil uranium dioxide core. Enrichments range up to 3.4 percent U_{235} . The active lengths of the fuels approach 10 feet and the core cross sections are up to 7.6 inches square or a 11 inch diagonal. Several of the fuels contain internal hardware such as spacers, tube cladding material. For instance, the Piqua fuel is nominally aluminum clad, but contains internal and external stainless steel tubing for flow control.

FACILITIES

The major elements required for chemical reprocessing of power fuels are shown in Figure 2. Included are a dissolver for removal of the fuel cladding and conversion of the cores to aqueous nitrate media; clarification facilities to recover core material in the cladding removal solutions and to remove solids from the dissolved coresolutions; surge storage facilities; a pipeline for transfer of the solutions; a solvent extraction recovery facility; and facilities for storing the radioactive wastes produced by the reprocessing complex. The first three steps (dissolution, feed clarification, and storage) are to be provided by installation of new and revised equipment in the U Plant previously described. A new pipeline will be constructed to transfer solutions to the presently existing and operating Redox Plant for solvent extraction. Existing facilities will also be utilized for disposal of the liquid and dry wastes produced.

DISSOLUTION PROCESSES

Present Hanford philosophy for the dissolution of power fuels recommends the use of a two step process encompassing a cladding removal process followed by a core dissolution process with chemical conditions tailored to the fuel involved - as shown in Figure 3. Five processes are shown for the four cladding-core fuel combinations scheduled for Hanford. The dissolution processes generally involve highly corrosive boiling media, generate copious quantities of off-gases including ammonia and hydrogen, and the cladding removal solutions tend to attack core materials.

Zircalloy Removal

Further details on the recommended dissolution processes are shown in Figure 4. The Zirflex process is recommended for the removal of Zircalloy cladding from the two fuels scheduled for Hanford reprocessing. This process employs ammonium fluoride-ammonium nitrate mixtures for selective dissolution of Zircalloy without appreciable attack of UO_2 cores. Indicated dissolution rates of oxidized Zircalloy are in the range of 2 to 3 mils an hour requiring 10 to 15 hours to remove a 33 mil cladding. Although the presence of ammonium nitrate substantially

Fig. 2—Chemical processing plant.

DISSOLUTION PROCESSES		
<u>FUELS</u>	<u>CLADDING REMOVAL</u>	<u>CORE DISSOLUTION</u>
SSt / UO ₂	SULFURIC ACID	NITRIC ACID
Zy / UO ₂	AMMONIUM FLUORIDE	NITRIC ACID
Al / U-MO	SODIUM HYDROXIDE	NITRIC ACID FERRIC NITRATE
Al / UO ₂	MERCURIC NITRATE - NITRIC ACID (TOTAL DISSOLUTION)	

Figure 3

DISSOLUTION PROCESS CHARACTERISTICS*							
METAL	REACTANT	VOLUME GAL.	ATTACK RATE MILS/HR.	OFF GAS Cmpds	GAS SCFM	WASTE LOSS %	CYCLE TIME HOURS
Zy	NH ₄ F, 5.5 <u>M</u> NH ₄ NO ₃ , 0.5 <u>M</u>	1200	2-3	NH ₃ H ₂	100 2	<0.5	12
SSt	H ₂ SO ₄ , 4 <u>M</u>	1200	12	H ₂	38	<0.5	2
Al	NaOH, 3.3 <u>M</u> NaNO ₃ , 3.0 <u>M</u>	1000	10	NH ₃ H ₂ O	60 80	<0.1	4
UO ₂	HNO ₃ , 3 <u>M</u>	1200	10	NO ₂ H ₂ O	8 4	—	25
	HNO ₃ , 8 <u>M</u>	400	65	NO ₂ H ₂ O	95 47	—	4
U-Mo	HNO ₃ , 4 <u>M</u> Fe(NO ₃) ₃ , 1 <u>M</u>	1200	50	NO ₂ H ₂ O	220 150	—	2

* BASED ON 1 TON OF URANIUM

Figure 4

reduces hydrogen production, approximately 0.1 mole of hydrogen and 5 moles of ammonia are produced per mole of Zircaloy dissolved. It is proposed that plant operation will employ bleed-air to reduce the hydrogen below the lower explosive limit throughout the entire off-gas train, and to keep ammonia non-explosive until removal occurs in the condenser-scrubber system. As in the case of Sulfex, Zirflex solutions also attack core materials. Actual core losses are primarily determined by the solubility of uranium and by the efficiency of the removal of uranium particulates and entrained particles in the cladding waste solution. Positive steps should be utilized to minimize the presence of oxidants or hexavalent uranium.

Stainless Steel Removal

Dissolution of 304-L stainless steel in 4 M H_2SO_4 proceeds with a penetration rate of about 12 mils per hour, although the presence of actively corroding iron may be required to initiate the dissolution. Thus, approximately two hours will be required to dissolve the 21 mil Yankee cladding. Approximately 1 to 1.5 mols of hydrogen are produced per mole of stainless steel dissolved, requiring the use of an air or inert gas bleed to eliminate potential explosion problems in the off-gas system. The dissolution rate and solubility of UO_2 in 4 M H_2SO_4 are both much less than those for stainless steels. It is anticipated that such reaction solubility effects will limit uranium losses to the range of 0.1 to 0.5 percent for UO_2 cores. However, centrifugation of the coating waste may be required to recover uranium precipitates or particulate UO_2 . Since hexavalent uranium is reactive and soluble in sulfuric acid, adequate precaution such as flushing and correct equipment design must be employed to assure the removal of oxidants before cladding removal operations are initiated.

Aluminum Removal

The use of sodium hydroxide-sodium nitrate mixtures is recommended for selective removal of aluminum. Dissolution rates are in the range of 10 mils per hour requiring about 4 hours for the removal of the 40 mil Pathfinder cladding. This process produces approximately 0.25 moles of ammonia per mole of aluminum dissolved. Alternately, total dissolution of the cladding and cores of Piqua and Pathfinder fuels may be achieved by the use of mercuric nitrate catalyzed nitric acid-ferric nitrate mixtures.

UO_2 Dissolution

Uranium dioxide cores are readily dissolved in nitric acid. Dissolution rates vary considerably depending upon the history of the UO_2 and upon the concentration of nitric acid and uranyl nitrate in solution. Typical integrated rates of 10 to 70 mils per hour may be readily obtained. The off-gases produced are essentially nitrogen

oxides and require the presence of oxygen for acid recovery. Cores that powder or disintegrate to produce large surface areas will probably require the use of incremental acid addition techniques to limit maximum dissolution rates. No particular difficulties are expected in the storage, transfer, or plutonium oxidation of these solutions.

U-Mo Dissolutions

Uranium-molybdenum core alloys can not be dissolved in nitric acid without precipitation problems. However, the addition of ferric nitrate to the nitric acid accelerates dissolution rates and minimizes precipitation problems. Dissolution rates of uranium-molybdenum alloys in such mixtures are relatively high, i.e., 50 mils per hour. Incremental additions of reagents is also indicated to avoid exceeding the capacities of the off-gas system. Again the primary constituents in the off-gas are nitrogen oxides. The dissolver solutions appear to be stable and do not precipitate on standing. Oxidation of plutonium by dichromate proceeds normally in such solutions. However, the ferric nitrate-nitric acid-sodium dichromate system is relatively corrosive and optimum conditions must be found to minimize corrosion if the oxidizer is to be constructed of 304 stainless steel.

Passivation Problems

During exposure of Zircaloy clad fuels to high temperature water, a film of oxide forms on the cladding. This oxide is highly resistant to attack by ammonium fluoride solutions and dissolution occurs through a pit type penetration as shown in Figure 5. Notwithstanding, dissolution of an oxidized 30 mil cladding is completed in 10 to 15 hours. Stainless steel also tends to form a passive surface during reactor exposure. However, the combination of preheating the dissolver, the presence of small amounts of carbon steel, and contact of the fuel elements with construction materials such as Hastelloy or Ni-iron appears to prevent any deleterious effects. Only small quantities of nitrate contamination in the sulfuric acid grossly aggravates the passivation problems.

CRITICALITY PROBLEMS

The processing of enriched uranium leads to problems of criticality that are not encountered when natural uranium is processed. Criticality problems arise in heterogeneous metal-liquid systems for enrichments greater than that natural uranium and in homogeneous systems for enrichments above 0.94% U_{235} . Nuclearly safe dissolver operation may be assured by use of one or more of the following techniques.

1. Geometric limitations where the maximum dimensions of the equipment are such that fissile materials can not develop a

nuclearly critical geometry.

2. Batch operation where the quantity of material handled is confined to a batch less than minimum critical size.
3. Concentration control where operating safeguards are employed to limit the maximum concentration to safe levels.
4. The use of soluble poisons such as boron to provide for neutron capture within the solutions.

Of these four techniques, only geometric systems provide a positive safeguard against administrative or operating errors. Figure 6 indicates the permissible geometries of cylinders, slabs and rectangles as a function of U_{235} enrichment. It will be noted that at 5% U_{235} enrichment, the maximum permissible cylinder diameter is 7.8 inches, the maximum slab thickness is 2.9 inches, and the maximum permissible area of a rectangle or square is 47.8 square inches. Thus, rather small equipment is indicated for the portion of the dissolver handling heterogeneous solutions. As a matter of interest, the estimated always safe concentration is 250 grams of 5% U_{235} per liter.

DISSOLVER CONCEPTS

Two dissolver concepts which employ geometric limitations for criticality control are shown in Figure 7. The concepts embrace a heterogeneous criticality philosophy since it has been assumed that disintegration of the cores may result in UO_2 fines permeating the entire dissolver. Both concepts employ the use of a slab reservoir constructed in straight line, serpentine or folded-around construction to secure the large solution volume required. Alternate geometries are shown for the metallic fuel crib. The first is a vertical, cylindrical crib. The second is a horizontal trough crib. Current information indicates the capacity of a single crib to be about 25 tons of uranium per year, thus in application, a multiple number of cylinders or troughs will be employed to multiply the permissible charge to a maximum commensurate with cell limitations. Solution turn over between the reservoir and crib will require a transfer device such as gas lift, an air pressure pump, or deepwell turbine pump. Current estimates indicate that either cylinders or troughs with associated reservoir volume scaled at 1,000 gallons per ton of uranium charge can be "shoehorned" in a U Plant cell. Theoretically at least, the dissolver installation in which the crib operates as a well-stirred tank, and the reservoir in plug-flow pattern show promise of maximum dissolution rates - approaching 75 to 85% of those obtainable in a common batch system.

No foaming problems appear to be present in any of the recommended processes, and more or less conventional disengaging devices may be

Fig. 5—Oxidized and partially dissolved Zircaloy-2.

Fig. 6—Criticality parameters.

utilized. The disengaged off-gases will proceed through a condenser for nitric acid recovery, through a scrubber for final off-gas clean up, iodine removal, and ammonia removal, and finally through a filter for particulate removal before discharging to a stack system.

Materials of Construction

The highly corrosive nature of the proposed dissolution media, particularly sulfuric acid and nitric acid-ferric nitrate obviates the use of conventional materials for dissolver construction. The construction material utilized must withstand liquid, interface and vapor corrosion of the five processes previously outlined. It must not offer any exceptional fabrication difficulties, it must have adequate structural strength to withstand expected mechanical shocks, and it should not deteriorate significantly under the radiation environment. The need to withstand mechanical shock such as dropped fuel elements, etc., precludes the use of thin noble metal claddings and the need to withstand high radiation field eliminates any known plastic as a material for construction. The two candidates shown on Figure 8 are only typical of the family of high nickel-chrome alloys that are being surveyed for use. The corrosion rates cited are for an integrated fuel cycle employing boiling solutions. Corrosion rates for heat transfer surfaces may be 3 to 5 fold higher. For Sulfex conditions only, Ni-o-nel welded with Ni-o-nel would be the best construction material. Hastelloy F has somewhat better resistance to the fluoride solutions encountered in the Zirflex process. For these reasons, vacuum melted Hastelloy F base material welded with Ni-o-nel is recommended at this time as the preferred construction material.

FEED CLARIFICATION, STORAGE, AND TRANSFER

All solutions exiting the dissolver will be clarified in a critically safe centrifuge. This technique will recover any uranium precipitates or fines present in the cladding removal or core dissolution solutions, and will remove any obnoxious solids in the latter. Supernatant liquid and slurries leaving the centrifuge will be collected in geometrically safe slab tanks, sampled to determine uranium and plutonium content, and material with recoverable, valuable constituents recycled to the dissolver. The clarified solutions will be diluted to always safe concentrations (0.9 M UNH for 5% enrichment and 1.65 M UNH for 3% enrichment) and forwarded to a precisely calibrated tank for accountability measurements before transfer to the surge storage tanks. During storage, temperatures, liquid levels, solution composition, etc. will be monitored to avoid hazardous off-standard conditions. Upon demand, perhaps for two campaigns per year, the stored solutions will be transferred to Redox for solvent extraction through the core of a direct buried, cathodically protected, concentric pipeline. The

Fig. 7—Dissolver concepts.

PROCESS	CONSTRUCTION MATERIAL			
	ESTIMATED CORROSION RATE, MILLS / MONTH			
	CRIB		RESERVOIR	
	HASTELLOY-F	Ni-o-nel	HASTELLOY-F	Ni-o-nel
ZIRCALOY REMOVAL	1.1	2.0	1.2	2.4
SS† REMOVAL	1.4	0.4	1.6	0.5
UO ₂ DISSOLUTION	1.0	1.0	1.0	1.0
U-Mo DISSOLUTION	—	—	5.0	—

Figure 8

annular portion of the pipeline will be routinely monitored to detect leakage.

SOLVENT EXTRACTION

The valuable fissile and fertile materials in the dissolver solutions will be recovered in the Redox solvent extraction battery. Figure 9 shows a cutaway of this plant. You will note the typical Hanford cell construction and the use of remote installation and equipment removal techniques. The reprocessing of NPF fuels is to be accomplished in this Plant in addition to its normal production duties. Solvent extraction of solutions from power fuels will require approximately 25 to 30 operating days.

The basic Redox solvent extraction battery includes a decontamination cycle preceding a partition cycle and final uranium and plutonium decontamination cycles. In this respect the Redox process is quite similar to the well-known Purex process. However, Redox utilizes hexone (methyl isobutyl ketone) in lieu of tributyl phosphate and employs an aluminum nitrate salting agent in lieu of nitric acid. The Redox process also obtains its best decontamination when employing an acid deficient feed stock.

The solvent extraction feeds prepared from UO_2 cores will have much the same characteristics as those prepared from metallic uranium. However, power fuel feedstocks will contain higher concentrations of fission products and fissile materials than those normally experienced. Nuclear safety will be maintained by limiting uranium concentrations to nuclearly safe values even under reflux conditions in columns and during concentration steps.

Feed stocks prepared from U-Mo alloys will pose additional problems since solutions are and must remain acidic to avoid precipitation problems. Thus a decontamination loss will be experienced over the first decontamination cycle, but should be partially recovered in later cycles or by the use of tail-end treatments such as silica gel, anion exchange, etc. No emulsion difficulties have been noted in laboratory studies due to the molybdenum present nor has the presence of trace amounts of sulfate or fluoride appreciably affected solvent extraction behavior or equipment corrosion.

WASTE DISPOSAL

All steps (receiving and storage, mechanical reprocessing, dissolution, feed clarification, solvent extraction) in the reprocessing complex will produce dry or liquid radioactive wastes. These wastes are potentially highly toxic and some of them must be contained in a safe and economic manner for periods ranging up to hundreds of years. Fortunately climatic and geological conditions at Hanford permit the

Fig. 9—Cutaway of Redox plant.

Fig. 10—Waste storage facility arrangement.

use of rather simple tanks for liquid disposal as shown in Figure 10. These tanks are constructed of concrete with carbon steel liners and are equipped with the necessary ancillaries for adequate monitoring and removal of heat generated by radioactive decay.

Research and Development studies are in progress to determine optimum techniques for the disposal of the liquid wastes from this program which are outside the realm of production experience, i.e., the sulfate, fluoride, and molybdenum solvent extraction solutions. No prohibitive problems appear evident although it may be desirable to postpone neutralization of some of the wastes until just before discharge into the tanks.

In closing I would like to briefly acknowledge the contributions by a large number of personnel from which this brief resume' was extracted.

MEASUREMENTS

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ABSTRACT

Hanford plans for the measurement of the nuclear materials content of non-production fuels are presented. A comparison of the expected reliability of calculated and measured values which will be obtained at various points in the over-all fuel cycle is made. Some of the key factors in the problem of reconciling values obtained at the various points are discussed.

INTRODUCTION

One of the key areas of concern in the non-production fuels (NPF) reprocessing program is that related to the determination of the fissile material content of the spent fuel elements. The concern stems primarily from the large monetary values assigned to the fissile materials. For instance, the spent reactor charges slated for processing at Hanford, although relatively low in uranium enrichment, will contain uranium and plutonium with assessed values of perhaps one-half to several million dollars per charge. Consequently, a small uncertainty in the measurement of the uranium and/or plutonium content may represent materials worth many thousands of dollars. This paper is presented with a two-fold objective in mind: to discuss Hanford plans for receiver measurements of NPF materials to be processed here, and to indicate some of the factors of importance in the problem of reconciling the measurements which will be made at various points of the over-all non-production reactor fuel cycle.

NUCLEAR MATERIALS CONTROL COMPLEX

Figure 1 presents a diagram of the entire nuclear materials control or measurements complex for non-production fuels. The cycle originates with the fuel element fabricator, who has the opportunity, at least, to get an accurate value for the composition of his product.

FIGURE 1

NUCLEAR MATERIALS CONTROL COMPLEX FOR NON-PRODUCTION FUELS

The next measurements responsibility lies with the reactor operator. The accuracy of his measurements of reactor power levels, fuel rod exposure, and various reactor parameters will determine the accuracy of his calculations of uranium-235 burn-out, plutonium production, etc. Whatever his degree of accuracy, his calculations will serve as the basis for his estimate of the total uranium, uranium-235, and plutonium delivered to the fuel reprocessor.

With the present state of the art, the uranium and plutonium content of the spent fuels cannot be measured by non-destructive means. Rather, it will be necessary to dissolve the material and assay the resulting solution for uranium and plutonium. One of the by-products of the bulk plutonium and uranium measurements will be the data obtained on the plutonium-to-uranium ratio and on the uranium and plutonium isotopic composition of the spent fuels. These data will be helpful to the reactor operators in refining their calculations of burn-up and plutonium production. They will also be helpful in reconciling differences between calculated and measured plutonium values.

HEAD-END MATERIALS CONTROL PROBLEMS

Since the fuels cannot be assayed until they have been dissolved, the processing steps which precede dissolution must be considered in any discussion of reprocessing plant materials control. As described in previous papers, the head-end and dissolution system to be used at Hanford will probably include the steps shown in Figure 2. The diagram also shows a rough estimate of potential material hold-up, and consequent diversion to side streams for ultimate recovery or disposal to waste, for each of the head-end steps. It is felt that such hold-up and diversion, in any case in which it occurs, is certain to contribute significantly to the over-all measurement uncertainty.

The problem of materials control through the head-end will vary in magnitude with the chemical and structural make-up of the fuel elements and with the details of the procedures finally used. If, for instance, the mechanical treatment does not extend beyond hard-ware removal, no loss or hold-up at this point should result. On the other hand, if the elements are cut into pieces, a significant part of their contents may remain in the shearing equipment as a sludge. In this event, the ultimate measurement uncertainty will be affected by the operational ability to clean out the equipment and get the residues into a measurable form. A rough estimate is that generally not more than one per cent of the material processed will be diverted from the main stream at this point, although there may be some instances in which the hold-up and diversion will be considerably greater.

Somewhat the same considerations affect the core dissolution step. In this case, it is conceivable that the standard dissolving procedure established for a given fuel element may occasionally leave an appreciable amount of the core undissolved. The non-standard conditions associated with clean-out of the dissolver in such a case will also contribute to the uncertainty of the over-all measurement, even though the clean-out solutions will be assayed. It is estimated that generally not more than five per cent of the material will be subjected to this off-standard treatment.

FIGURE 2

NUCLEAR MATERIALS CONTROL FOR THE HANFORD DISSOLUTION
OF NON-PRODUCTION FUELS

One step, decladding, has been left out in the discussion so far. It is believed that chemical decladding will give only a small loss, and one which can be measured.

It is hoped that experience will prove that the estimates of hold-up and diversion discussed above are overly pessimistic. At the same time, it is felt that the problems in materials control during mechanical treatment, decladding, and dissolving will contribute much more to the uncertainty of the over-all measurements than will the problems in solution volume measurement and assay.

HANFORD PLANT SOLUTION MEASUREMENTS

In this discussion of Hanford receiver measurements of NPF fuels, the emphasis will be placed upon the determination of total uranium and plutonium in dissolver solutions. Hanford's concern with these particular assays stems from the factors that 1) low enrichment uranium fuels, with a significant plutonium content, will be processed here, and 2) in spite of the difficulties in working with the highly radioactive dissolver solution, this is the only point in the reprocessing system where samples representative of a particular batch of fuel elements can be obtained. Because of the large size of the Redox plant separations equipment, it is not practical to completely segregate the dissolved fuels from the various reactors during the reprocessing operation. Hence, in spite of any special processing and clean-out precautions that might be taken, a sample from any point beyond the dissolver solution feed system will potentially represent a blend.

The above comments have stressed the assay of dissolver solutions. The complete materials control system will, of course, include the necessary assay of pertinent flush and waste streams.

Head-End Routing System For Dissolver Solutions

Figure 3 shows the tentative Hanford routing system for dissolver solutions and head-end clean-out flushes. It has been proposed that from the dissolver, the solution will be moved through a centrifuge into a slab tank for preliminary estimation of uranium and plutonium content for critical mass control. The obvious difficulties in mixing and sampling the contents of the slab tank make it impractical to use this vessel for the primary dissolver solution sample point. Rather, the next vessel in the series, which will probably be sized to hold the solution from about three tons of uranium, will be equipped for sampling and volume measurement (see Figure 4).

Sampling

The problem of taking and handling dissolver solution samples is complicated by the high radiation levels. The radiation hazard will be reduced by pulling solution from the vessel into a remote sample cup (Figure 4), from which the desired amount can be removed. In order to assure that the small sample, which may range in size from one ml to several hundred ml, will be truly representative of the solution, a

FIGURE 3
HANFORD HEAD-END ROUTING SYSTEM FOR DISSOLVER SOLUTIONS

FIGURE 4
HANFORD SOLUTION VOLUME MEASUREMENT AND SAMPLING

definite sampling procedure will be established and thoroughly tested. The procedure will include provisions for thorough mixing of the vessel contents by agitation for a specified length of time. The solution will be recirculated through the sample cup for an adequate, specified period. Test samples will be taken and analyzed before the final bulk sample, probably 20 ml in volume, is taken. As a verification of sampling accuracy, the measured specific gravity of the sample may be compared with the specific gravity of the solution measured in the plant vessel. Past tests in plant equipment have shown that sampling can be made very accurate.

Volume Measurement

Volume measurements will be made with a high precision dip tube and manometer system, using well-established techniques which have seen long and satisfactory use at Hanford in similar applications. With the equipment shown schematically in Figure 4, determination of the pressure differential between the bottom dip tube and the top of the solution will give a measure of the weight of liquid in the tank. The weight may be converted to volume using the solution specific gravity, determination of which can be made either in the laboratory or in the vessel itself from the pressure differential between dip tubes at different depths of liquid.

The accuracy of the volume measurements will depend upon the care with which the volume calibrations are made and the extent to which the internal vessel geometry remains constant between calibrations, as well as upon the accuracy of the specific gravity measurements and such corrections as are necessary. Past experience at Hanford has indicated that under actual plant operating conditions, an individual volume measurement is accurate to only about one to two per cent. This situation has been the subject of a recent investigation by personnel of the Chemical Development Sub-Section, Hanford Laboratories^(1,2). They found that under carefully controlled conditions, the volume measurement accuracy shown in Table I may be achieved. These data, obtained with a 3000 gallon, cold process tank, a conventional dip-tube system, and a high precision manometer, show an over-all accuracy of 0.3 to 0.4 per cent to be obtainable for a single volume determination. Using the same tank for a lengthy period and making many calibrations and many measurements, the over-all accuracy may be as good as ± 0.15 per cent. It should be emphasized again that this represents an ideal case and one which it may not be feasible to realize in actual practice.

Analytical Procedures

One of the major problems in analytical work for a nuclear fuels reprocessing plant is the provision which must be made to protect personnel from the high radiation levels associated even with small samples. The usual solution is either to work with minute aliquots which require little shielding, or else to set up the complex equipment which will make it possible to handle large samples behind adequate shielding. The Redox analytical laboratory, which will handle the bulk of the Hanford NPF analytical work, is set up on the former

TABLE I

VOLUME MEASUREMENT ACCURACY ATTAINABLE WITH A
HIGH PRECISION DIP TUBE - MANOMETER SYSTEM

Nominal Tank Level Gallons	Estimated Accuracy of Single Measurement - 95% C.L. Relative Per Cent ^(a)					
	One Tank Calibration			Three Tank Calibrations		
	Overall	Random	Systematic	Overall	Random	Systematic
500	0.62	0.56	0.28	0.58	0.56	0.16
1000	0.47	0.40	0.24	0.42	0.40	0.14
2000	0.36	0.28	0.24	0.30	0.28	0.14
3000	0.33	0.22	0.24	0.26	0.22	0.14

- (a) Estimated volume measurement accuracy for an inventory type measurement. Estimated accuracies for a transfer type measurement are approximately the same. Values given in the table are based on experimental measurements using a 3000 gallon Hanford process tank, a conventional two line dip tube system, and a high precision manometer.

basis, with shielded containers for transferring and storing the relatively large plant samples and the analytical methods designed for very small samples. For instance, many solution assays are run on primary solution aliquots as small as 5 to 10 microliters. As a result, a 20 ml bulk sample should suffice for any anticipated set of dissolver solution assays.

Sample Handling and Analytical Control

Analytical Laboratory operational procedures and controls are indicated in Figure 5. The sampling operation in the plant will be carried out by a chemical operator using an established procedure. The analytical determinations will be run in the control laboratory by laboratory assistants and technologists working under the direction of supervisors and chemists and using well-tested procedures. Control of analytical quality will be maintained by having individual analysts umpire each other and by having synthetic standard samples run. The results from the umpire and standard sample determinations will be used for statistical determination of analytical precision and accuracy.

Analytical Methods

Basically, two approaches will probably be followed in the assay of dissolver solution for uranium and plutonium: 1) determination of the desired constituent in the primary sample itself, in which case the method must be specific or else the necessary corrections for interfering materials must be known; and 2) quantitative separation of the desired constituent from the bulk of the sample, and subsequent assay.

The NPF analytical methods which look the most promising at present for application at Hanford are described briefly in Table II. For uranium assay, the choice between the two methods listed will depend upon the composition of the solution to be analyzed. In those cases in which the solution is free of interfering substances, such as molybdenum, the controlled potential coulometer may be used for direct uranium determination.⁽³⁾ For this instrument, a sample containing from 4 to 10 milligrams of uranium is preferred. The coulometer works through the reduction of uranium(VI) to uranium(IV) at a mercury cathode, by the passage of current through the cell holding the solution at a constant, pre-determined potential. The applied potential may be adjusted to give essentially complete reduction of the uranium with minimum interference from other reducible constituents of the sample. The total current used for the reduction is measured by an electrical integrating system. The instrument has also been adapted to the determination of plutonium, by way of the plutonium(III) - (IV) change in oxidation state⁽⁴⁾. The big advantage of this instrument in these applications is the small size of sample required.

The second method for uranium, which has seen extensive use at Hanford, involves the isolation of the uranium from interfering substances by solvent extraction. The uranium in a 50 microliter sample is extracted into a TBP-hydrocarbon solution, and its concentration in the organic phase determined from the extent to which the sample

FIGURE 5
SAMPLE HANDLING, ANALYSIS, AND QUALITY CONTROL

TABLE II

ANALYTICAL METHODS

<u>Constituent</u>	<u>Description</u>	<u>Standard Deviation, Relative Per Cent</u>	
		<u>Random Error</u>	<u>Systematic Error</u>
Uranium	Direct determination by controlled potential coulometer.	± 0.5	± 0.1
	Isolation of U by TBP extraction - U determined by X-ray absorption.	± 1.0	± 0.1
Plutonium	Isolation of Pu by anion exchange - Pu determined by controlled potential coulometer.	± 1.0	± 0.1
	(a) Radio-assay: alpha count of solution aliquot in combination with plutonium specific activity factor.	± 2.0	± 0.2
Specific Gravity	Falling Drop	± 0.3	± 0.07
U-235	Isolation of U by solvent extraction - U-235 determined by mass spectrometer.	± 0.10	± 0.025

(a) Secondary method used for process control or as verification of primary method.

reduces the intensity of an incident X-ray beam.

Two methods will also be available for plutonium assay. In the primary method, the first one listed in Table II, the plutonium present in the dissolver solution sample is quantitatively separated from interfering substances by anion exchange⁽⁵⁾. The product solution, containing about 150 micrograms of plutonium, is then assayed for plutonium with the controlled potential coulometer. A secondary method, which will be useful for process control or in verification of the primary method, makes use of conventional radioassay procedures. In this method, which has been used for many years, the alpha emission rate of an aliquot is determined, corrected for extraneous alpha activities such as those from uranium, americium, and curium, and converted to plutonium concentration by use of the plutonium specific alpha activity. This is a simple, very useful method if the specific activity is known. However, the isotopic composition and the specific activity of reactor-produced plutonium depend upon the conditions of reactor design and operation. Consequently, accurate determination of plutonium in NPF dissolver solutions by radioassay will require measurement of the specific activity for each dissolver solution batch. Either of two methods will be available for the specific activity determination: 1) calculation from the plutonium isotopic composition; and 2) direct measurement on a purified sample, of the plutonium, by determination of the alpha emission rate of a chemically assayed solution. In the isotopic concentration method, plutonium is separated from interferences by an anion exchange procedure. Mass numbers 239, 240, 241, and 242 are then determined with a surface ionization mass spectrometer (a 10 microgram sample is required), and mass number 238 is determined by alpha energy analysis.

The specific gravity determination listed in Table II, which will be necessary for the plant volume calculation, will be carried out in the laboratory by the highly reliable falling drop method. In this method, a five microliter drop of the aqueous sample is allowed to fall through a measured depth of organic solution of known density. The time of fall is then correlated with the specific gravity of the sample.

Uranium-235 determination will be made as indicated, probably with the conventional "uranium hexafluoride" type mass spectrometer, on material separated from the dissolver solution by solvent extraction.

Besides the description of the analytical methods, Table II shows an estimate of the uncertainty which will be associated with a single determination by each of the methods listed. The standard deviation is shown as arising from two components, the random error and the systematic error. The random error can be reduced in magnitude by repetition of the analysis, while the systematic error cannot. It represents the limit of accuracy obtainable regardless of the number of repetitive analyses. It will be noted that by running enough determinations on a sample, any of the methods is good to 0.1 to 0.2%.

Over-All Precision for Dissolver Solution Measurements

Precision Estimates

Previous sections have discussed the reliability of volume measurements and of pertinent analytical methods. Table III contains estimates of the reliability of over-all dissolver solution measurements when carried out under very carefully controlled conditions. Since it is common experience for chemical analysts to have those depending on their measurements ask for multiple repetitive analyses, Table III also shows the effect of repeated analysis upon precision. These estimates are derived for the case of a single volume determination on a single batch of dissolver solution. They show that although a marked increase in the precision at the 95% confidence level (C.L.) can be achieved by making several analyses, little additional benefit will be realized from a large number of analyses. They also show that, at best, because of the relatively large error in volume determination, the over-all precision of a single batch measurement will not be better than about $\pm 0.5\%$.

The estimates of over-all precision in Table III are optimistic, since they are based on a standard deviation of $\pm 0.2\%$ for a single volume determination, a value considerably better than any achieved under actual plant conditions at Hanford. The assigned contributions of the analytical uncertainty to the over-all precision are taken from the table of analytical standard deviations, Table II, and are probably realistic. The precision statement given for a particular number of analyses includes the analysis of an equal number of standards and the application of individual standard recovery values to individual sample results.

In calculating the values shown, no consideration was given to multiple volume determinations. Although a reduction in the random error component of the volume determination uncertainty might be realized by sampling and measuring the volume before and after diluting the vessel contents, it is not felt that the small improvement in reliability would justify the cost of extra sampling, etc. Much more is to be gained by repeating the analysis a few times.

Economic Considerations

In establishing the criteria for any measurements system designed to provide a basis for payment for material transferred, consideration should be given to the relation between the costs of measurement and the value of the material being measured. Table IV shows the results of an attempt to do this for the NPF dissolver solution measurements now under discussion. In this table are presented single-batch measurement precision estimates, estimates of measurement costs for varying numbers of analyses, and an estimate of the dollar value of the associated uncertainty in total plutonium or uranium measurement. The precision estimates are taken from Table III. Measurement costs were calculated on the basis that the cost for the first analysis would include the fixed and overhead costs which would be incurred regardless of the number of analyses run. The estimated costs for repetitive

TABLE III

VARIATION IN OVER-ALL MEASUREMENT PRECISION
WITH REPETITIVE ANALYSES FOR A SINGLE BATCH
OF HOMOGENEOUS SOLUTION

<u>Constituent</u>	<u>Analytical Method</u>	<u>Number of Analyses</u>	<u>Over-all Measurement Precision, 95%C.L.^(a)</u>
Uranium	Direct determination by controlled potential coulometer.	1	± 1.49
		4	± 0.85
		8	± 0.69
		∞	± 0.47 (b)
	Isolation of U by TBP extraction - U determined by x-ray absorption.	1	± 2.9
		4	± 1.49
		8	± 1.11
		∞	± 0.47 (b)
Plutonium	Isolation of Pu by anion exchange - Pu determined by controlled potential coulometer.	1	± 2.9
		4	± 1.49
		8	± 1.11
		∞	± 0.47 (b)

(a) The 95% confidence level for the bulk measurement of a single batch of dissolver solution using the estimated analytical precisions given in Table II, and a volume measurement standard deviation of $\pm 0.2\%$. The precision statement given for a particular number of analyses includes the analyses of an equivalent number of standards and the application of individual standard recovery values to individual sample results.

(b) The 95% confidence level for an infinite number of analyses for a single batch measurement of dissolver solution assuming a single batch volume measurement precision of $\pm 0.4\%$ at the 95% C.L.

TABLE IV

ECONOMIC CONSIDERATIONS: MEASUREMENT COSTS VERSUS DOLLAR VALUES
OF RESULTING SINGLE BATCH SOLUTION MEASUREMENT UNCERTAINTIES

<u>Constituent</u>	<u>Number of Analyses</u>	<u>Single Batch Measurement Precision, 95% C.L.</u>	<u>Measurement Cost \$(a)</u>	<u>Measurement Cost % of Total Value (b)</u>	<u>Dollar Value of Uncertainty</u>
Uranium	1	± 1.49	300	0.2	2235
	8	± 0.69	500	0.33	1035
	∞	± 0.47	---	---	705
Plutonium	1	± 2.90	300	0.2	4350
	8	± 1.11	600	0.4	1650
	∞	± 0.47	---	---	705
Uranium		$\pm 0.30^{(c)}$	150,000	100	450
Plutonium		± 0.30	150,000	100	450

- (a) Measurement cost of first analysis based on fixed cost of sampling and analyzing test samples, taking of bulk samples, volume calibration costs, preparation of laboratory standards, radiation monitoring service, etc. Cost for a number of analyses includes cost of analyzing an equivalent number of standard samples. Measurement costs should be considered only as approximate estimates.
- (b) Based on an assumed single batch of 3 ton U valued at \$100,000 per ton, \$50,000 for the uranium content and \$50,000 for the plutonium content.
- (c) Assumes an expenditure equivalent to the value of the material to reduce systematic errors as far as is technically feasible.

analyses include the cost of analyzing an equal number of standards. Uncertainty dollar values were derived from the assumption that a three-ton batch of uranium is measured, with an average total value of \$100,000 per ton - \$50,000 for the uranium content and \$50,000 for the plutonium.

On this basis, single analyses for uranium and plutonium in the three-ton batch of dissolver solution will give estimates of the monetary value as being \$150,000 $\pm$ \$2235 for uranium and \$150,000 $\pm$ \$4350 for plutonium. Making eight analyses for each, still with a single volume determination, will reduce the value of the total uncertainty for both materials from about \$6600 to about \$2700, at an added analytical cost of about \$500. Although it may be worthwhile to reduce the uncertainty by a limited number of repetitive analyses, the point is soon reached where nothing further is to be gained. As the data show, it would be possible to use the entire batch of solution for analytical measurements and still have an appreciable dollar value uncertainty.

Another approach was taken in deriving the bottom set of numbers. Here, it was assumed that an expenditure equal to the value of the material might suffice to reduce the systematic error as far as was considered technically feasible. Even so, an appreciable dollar uncertainty would still be left.

It should be remembered that these uncertainty values can be either plus or minus. Consequently, one of the parties to the shipper-receiver transaction might wish to pay the added cost of extra analyses so as to reduce the uncertainty, only to find that the improved measurement favors the other party.

Summary of Measurement Precision Estimates

The above discussion has described what can probably be done in the way of measurements of dissolver solution, provided those governing the situation want to spend the money necessary to do it. Table V presents a summary of measurement uncertainties, in terms of the range of precision (95% C.L.) that can probably be obtained in practice without excessive expenditure. The range in analytical precision has been estimated at $\pm 0.2 - 0.6\%$ for uranium and plutonium. The same volume measurement uncertainty, of from 0.2 to 1% is given for all three constituents. Any of these precisions may be insignificant in the over-all measurement, if much of the material is held-up or diverted to side-streams during the pre-dissolution operations.

Long-term Measurement Precision

Thus far, consideration has been given only to single-batch measurements. It has been shown that, although careful control and the use of many repeated analyses may make possible a single-batch measurement precision (95% C.L.) of $\pm 0.5\%$, the benefit to be derived hardly seems to warrant the cost. A better approach, at least for the spent fuel from a large reactor, appears to be to take advantage of the low cost and high measurement precision obtainable over many

TABLE V
MEASUREMENT UNCERTAINTIES
(95% C.L.)

<u>Constituents</u>	<u>Analytical</u>	<u>Volume Measurement</u>	<u>Over-All (Incl. Mat'ls Handling)</u>
Total U	± 0.2 - 0.6	± 0.2 - 1.0	± 0.30 - 2
U-235	± 0.05 - 0.25	--	± 0.30 - 2
Pu	± 0.2 - 0.6	--	± 0.40 - 2

batches, with only a few analyses per batch. This is done in Table VI.

The calculations in Table VI are based on the assumptions of an 18 ton per year discharge rate and a three ton batch size. Under these conditions, four uranium analyses per batch will give a measurement precision (95% C.L.) of $\pm 0.49\%$ for the 18 tons. Running a tank calibration for each batch will give only a slight improvement in precision. Extending the precision calculation to cover a five year period, with six batches per year and one tank calibration per year, gives a precision estimate of $\pm 0.31\%$. Table VI also presents the same type of considerations for plutonium. These numbers emphasize the measurement cost advantages of depending upon the long-term precision to even out any short-term discrepancies.

RECONCILIATION OF SHIPPER AND RECEIVER MEASUREMENTS

Reliability of Measurements Throughout the Nuclear Materials Control Complex

Now that the Hanford NPF measurements system and problems have been presented in some detail, the groundwork has been laid for a comparison of the probable reliability of measurements throughout the NPF nuclear materials control complex. This comparison is made because for each fuel shipment, the shipper will state his estimate of the plutonium and uranium content. The reliability of that estimate will be of concern to the reprocessor, since it will govern to some degree the extent of his effort to check it. Figure 6 presents such a comparison for the fuels which are now scheduled for reprocessing at Hanford.

First, it will be noted that a precision (95% C.L.) of $\pm 0.1\%$ has been listed for the fuel element fabricators' measurement of total uranium. In informal contact with the fabricators, assurance was given that this degree of materials control is possible in their fabrication operation. This applies both to the uranium oxide fuels which will be the bulk of the Hanford reprocessing load and to the uranium-molybdenum alloy elements being fabricated for the Piqua reactor.

TABLE VI

LONG TERM SOLUTION MEASUREMENT PRECISIONS
FOR MATERIAL FROM A SINGLE REACTOR

<u>Constituent</u>	<u>Number of Analyses</u>	<u>Number of Dissolver Solution Batches (a)</u>	<u>Number of Tank Calibrations</u>	<u>Over-all Measurement Precision, 95% C.L. Relative Per Cent (b)</u>
Uranium	24	6	1	± 0.49
	24	6	6	± 0.41
	120	30	5	± 0.31
Plutonium	24	6	1	± 0.70
	24	6	6	± 0.66
	120	30	5	± 0.39

(a) One dissolver solution batch is assumed to be 3 tons U.

(b) Precision limits are based on analytical precisions given in Table II and the assumption that an equivalent number of standard solutions are analyzed for bias control and that each sample value is corrected by the recovery obtained on the standard. A volume systematic error of ±0.28% (95% C.L.) which reduces by the square root of the number of tank calibrations is assumed.

FIGURE 6

RECONCILIATION OF NUCLEAR MATERIALS VALUES THRU THE
NON-PRODUCTION FUELS CONTROL COMPLEX

For low enrichment uranium, and with input total uranium figures good to $\pm 0.1\%$, it should be possible to calculate the total uranium content of the spent fuels quite accurately. With a total uranium burn-out of only one or two per cent, even a large error in burn-out calculation will give only a small total uranium uncertainty, here estimated as $\pm 0.2-0.5\%$. Unfortunately, the same can't be said for uranium-235 and plutonium content. It has been estimated by Hanford physicists that for the first material discharged from a reactor of new design, the calculation of uranium-235 and plutonium content will be good to only $\pm 2-4\%$ and $\pm 5-10\%$, respectively. Once experience is gained with a reactor, and measurements of uranium and plutonium isotopic compositions and plutonium-to-uranium ratio are fed back into the reactor calculations, the calculations should improve. However, the uncertainties of reactor power measurement are such that it is unlikely that even with experience, the precision of the calculations of U-235 and plutonium content will be better than $\pm 1-2\%$ and $\pm 3-5\%$, respectively.

As shown in Table V, the over-all reliability of the Hanford reprocessing measurements is estimated, again in terms of precision (95% C.L.), as being about $\pm 0.3-2\%$ for total uranium, total plutonium, and total uranium-235. Since these numbers include the contribution from potential unmeasured losses in the head-end system, before the fuels are dissolved where they can be measured accurately, the uncertainty will be weighted on the negative side - that is, the reprocessor is likely to show less than the true value.

Thus it has been estimated that it may well be possible to calculate the total uranium more closely than the reprocessor can measure it, whereas the reprocessor's values for the uranium isotopic content and the total plutonium will be better than those obtained from reactor calculations. It is also worthy of note that if a highly reliable statement of total uranium can be obtained, the way is open for marked improvement in the reliability of the reprocessor's measurement of total plutonium, through application of the so-called "ratio method." In this case, the ratio of plutonium to uranium is determined in the dissolver solution, and the ratio applied to the total uranium figure to give a value for total plutonium. Thus, the solution volume does not enter into the calculation, nor is the method materially affected by possible unmeasured losses in the dissolving process; and the principal sources of uncertainty become the chemical ratio determination and the calculation of total uranium. It has been estimated that a precision (95% C.L.) of $\pm 0.3-0.8\%$ for total plutonium is technologically obtainable with the "ratio method," provided the total uranium is known to $\pm 0.2-0.5\%$ (precision, 95% C.L.).⁽⁶⁾

The question of the possibility of independent verification may be raised. Obviously, the only reprocessor measurements which can be checked by an independent umpire are the analytical methods, which can be run on a sample of the dissolver solution. One of the major problems here is the small number of independent laboratories in this country with the facilities and the experience necessary to analyze this type of sample.

In umpiring the analytical work, it would be preferable to be able to use the determination of absolute concentrations. However, experience has shown that this is not reliable for solutions of this type, unless the umpire analysis is run very soon after the sample is taken, or unless extreme sample containment precautions are taken. The samples are inherently unstable because of the high radiation levels. They continuously produce gas which makes long-term containment in volumetric equipment difficult, and are generally troublesome to handle. It is felt that the determination of the ratio between constituents may be a much more reliable procedure. The ratio is independent of volume changes and will be affected only by non-equivalent changes in concentration of the constituents. The solution composition can be adjusted so as to prevent the latter from happening. Figure 6 shows the estimated reliability of ratio measurements in dissolver solution, and also indicates the feed-back of these measurements to the reactor operators for use in refining their calculations.

In conclusion, it may be constructive to review Handord's experience in reprocessing aluminum-clad, uranium-metal fuel elements from the Chalk River Reactor (Table VII). Nine batches of elements were dissolved and measured. The over-all uranium recovery was 99.6% of what was calculated to be there. The over-all plutonium recovery was only 94% of the predicted value. Although low, the latter is well within the estimated precision of the reactor calculations.

TABLE VII

HANFORD REPROCESSING EXPERIENCE: PREDICTED
VALUES VERSUS MEASURED VALUES FOR TOTAL
URANIUM AND PLUTONIUM IN CHALK RIVER SPENT FUELS

Shipment Number	Per Cent Found of Predicted Values	
	Uranium (a)	Plutonium
1	98.0	83.1
2	98.6	94.4
3	100.1	95.0
4	98.1	91.9
5	98.7	92.7
6	(89.9) (b)	(86.1) (b)
7	100.5	103.1
8	99.5	94.1
9	102.9	97.7
Average	99.6 (b)	94.1 (b)

(a) Major uncertainty in uranium bulk measurement believed to be due to uncertainties in the volume measurement.

(b) Large difference in shipment number 6 believed to be due to a gross error in bookkeeping. The values for number 6 not included in average.

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HANFORD QUESTION AND ANSWER SESSION

Baranowski:

We have received quite a few questions and I hope that they can be answered satisfactorily. I will answer a few and Messrs. Cooper, Zahn, Platt and Harmon will answer the remainder.

"Outline the procedures that the AEC will require for fuel elements known to be ruptured."

Response - Baranowski:

It is an extremely difficult problem, and we do not have a solution to it. It depends upon the type of fuel element as well, I believe, as the extent of the rupture and the subsequent release of fission products. Each shipment of fuel containing a rupture would have to be evaluated by the processing site to determine what would be required to unload the casks.

The cask acceptance criteria, which will be used in the negotiation of the processing agreement, does specify that the shipper must encapsulate ruptured elements. The encapsulating method must be approved by the processing site.

We recognize that there may be a problem of an undetected ruptured element. There may be a case where an element could be ruptured en route. We all are faced with the problem and, as I mentioned earlier, we do not have a good solution at this time.

"Are shipping cask unloading schedules available for each site?"

Response - F. Baranowski:

Assuming that you meet our cask acceptance criteria, it is expected that our processing sites can unload and return the containers to the F.O.B. point within a period of forty-eight hours. This may have to depend somewhat, I think, upon how you people design your casks, and how you agree with our methods of unloading

and handling containers.

The receiving and unloading operations are normally done only during the standard 40-hour week. Each Operations Office will provide to you, upon request, their present schedules for receiving commercial shipments, normal turn-around times, and estimated charges for off-shift operations of this type.

"Considering the possibility of large-scale saline water conversion plants using nuclear processed heat in Southern California, do you foresee no possibility for large shipments to Hanford? This seems an attractive possibility for the large cores required."

Response - V. R. Cooper:

I think that the only statement that I can make is in conformity with what I said earlier, that large shipments can be made to the Port of Pasco; that is the shipper's responsibility, and he will have to be responsible for transshipment to Hanford via truck or railway. I see no real obstacle in shipping a large core up the Pacific Ocean and up the Columbia River to Pasco, and then transshipping it, but then that would be strictly the reactor operator or his associate organization's responsibility.

"What is the maximum size barge that can traverse the Columbia's system to Pasco?"

Response - V. R. Cooper:

I am sorry, I am not an authority on that field. I can certainly get you that answer, and I have the gentleman's name and will see that he does get the information he seeks. Subsequent to the meeting the following information was obtained. Channel depth from mouth to Pasco has minimum depth of six feet except during May, June and July it is fifteen feet. After 1967 the minimum depth will be fifteen feet at any time. The maximum allowable barge dimensions are: 74 feet wide by 498 feet long.

"Will specifications be developed for fuel element canisters required for shipment in casks?"

Response - L. L. Zahn

Yes, they have been specified broadly already in the Hanford Cask Acceptance Criteria. We hope to be able to develop the more detailed part of the cask container design later in conjunction with the reactor operators. We should bear in mind that many functions of the cask container and other buckets which will be needed at Hanford to satisfy local processing requirements will be common; they

will both be designed to prevent accidental dropping of fuel element assemblies during handling, they both must satisfy the heat transfer requirements for cooling of the fuel element assemblies, and they both must satisfy nuclear safety. For this reason, it is felt that mutual advantages might be developed for the reactor operator and Hanford if the cask containers and storage buckets were of identical design to facilitate their interchange. We would wish, therefore, to be a party at least to commenting upon the design of the cask container; however, the broad specification now included in the Cask Acceptance Criteria is that some positive means of containment of the fuel element assembly must be provided.

"When are fuel elements removed from the transfer cans?"

Response - L. L. Zahn:

I assume that this question refers to the storage buckets which will be contained within the storage cells. If the fuel elements will be charged integrally to the dissolver, we would probably make the transfer from the storage bucket to the dissolver canister within the storage cell. The dissolver canister would then be transferred into the tank of another storage cell, which would be designed specifically to contain dissolver canisters. I mentioned how we are planning to handle trimmed and sheared fuel element assembly components from the mechanical cell. The dissolver canisters containing these components would also be stored within a storage cell designed specifically for dissolver canisters.

"What happens to ruptured fuel elements?"

Response - L. L. Zahn:

I mentioned some of the procedures we have in mind at Hanford to detect the presence of ruptured fuel elements within the cask before opening. We, of course, would view each situation involving a ruptured fuel element as representing an abnormality and we would have to, in each case, develop specific procedures for the situation. We could, for example, charge a ruptured fuel element assembly directly to the dissolver or to the mechanical cell. We would not wish to store a ruptured fuel element within our storage cells for any extended length of time.

"How many Dresden cores could be stored in your ten bathtub tanks?"

Response - L. L. Zahn:

I should emphasize that the racks of the storage tanks will be

designed to individual reactor requirements and will not necessarily be interchangeable between the various reactor fuels. We plan, therefore, to assign specific tanks to Dresden, Yankee, and so on. The number of assemblies that can be stored within any one tank will depend upon the design of the cask container and the storage bucket. As I mentioned earlier, the limiting capacity would be determined by heat transfer and nuclear safety conditions within the tank. We have made some conceptual designs of the storage rack for the Dresden fuel elements and have concluded preliminarily that approximately 25 tons of material can be contained within one tank.

"How would you disassemble fuel element assemblies into smaller sub-assemblies?"

Response - L. L. Zahn:

We plan to disassemble only one fuel element assembly, specifically that of Yankee. This assembly contains nine sub-assembly components held together by the end fittings and spacers and bands within the bundle. We plan to cut these bands with a special tool, perhaps a milling cutter or friction saw, operated from the main manipulator. The end fittings would be removed, of course, by the main saw.

"What is the assumed temperature in the dissolving solution for the attack rate quoted?"

Response - A. M. Platt:

I believe the question refers to Slide 4 which listed the composition of cladding removal solutions, composition of core dissolution solutions and some representative dissolution rates. Dissolution rates will vary over ten-fold from the initiation to the completion of the dissolution. The rates quoted were integrated values expected over the total dissolution process all at the solution boiling point. The solutions involved range from dilute to eight molar nitric acid and the actual temperatures are 5 to 15 degrees Centigrade above the boiling point of water.

"What is the solids capacity of the centrifuge?"

Response - A. M. Platt

We are negotiating with centrifuge manufacturers for the design detail of a critically safe centrifuge. Our current thinking is along the line of a continuous liquid and solid discharge centrifuge.

Under this system the holdup time would be the critical factor.

"Can you tell me what the \$300.00 per sample included in the assay schedule?" "Would this be the cost in routine analysis during the operation of your plant?"

Response - K. M. Harmon:

The \$300 for the first analysis is a rough estimation of the fixed cost associated with a single bulk measurement of this kind. It includes the cost of taking a series of test samples to insure that good sampling conditions exist, the cost of taking several large volume samples, the cost of maintaining equipment, and technical personnel, the cost of tank volume calibrations, and the cost of radiation monitoring etc. Basically it is an estimation, pro-rated on an individual sample basis, of the difference in cost involved in making measurements and making no measurements. As I indicated, you can get a relatively large number, say 8 to 10, of repetitive analytical measurements for the cost of getting set up to make a single measurement.

"I am still not clear on when the fuel gets separated from the cans, not the casks, but the cans. Can you remove the fuel from the cans when you are pulling the fuel out of the storage container, I mean out of the bath tub storage?" "When do you eject the fuel from the canister?"

Response - L. L. Zahn:

As I mentioned before, we hope that the cask container and the storage bucket will be of the same design. If so, the cask container would be removed directly from the cask and into the storage cell and an identical empty container inserted into the cask for return to the shipper. In this case, the fuel element assembly would be transferred to the dissolver canister from the storage bucket prior to dissolution. If the cask container and storage bucket were not interchangeable, an additional fuel element transfer would be needed to empty the cask container for return with the cask. These fuel element transfer operations between containers would be done within the storage cell or within the mechanical cell or perhaps even within the dissolver cell, but in any case, all fuel element transfers above deck would be within a container of some sort be it the cask container, the storage bucket, or the dissolver canister.

"Could you give us a little more detail on this shearing operation; is this after disassembly, or how do you do it?"

Response - L. L. Zahn:

I will elaborate some on the shearing operation. There are internal Hanford reports which describe this in far more detail than I would be able to cover at this time. Three related parameters have been found to be important in shearing; shear speed, shear blade geometry, and shear force. We have found that high shear speeds are more effective in separating fuel element assemblies. The controlling effect appears to be separation of the assembly by impact rather than by the more conventional shearing action. We have found also that the geometry of the shear blades has decided effect upon the force required to shear. Fundamentally, we view the shear as a mechanism for increasing the density of the dissolver charge to obtain higher dissolving rates. We would be taking rather short cuts, perhaps two or three inches, maybe even less, and the shear would make these cuts across the entire assembly as the feed mechanism moves it through the shear.

"Is this operation under water?"

Response - L. L. Zahn:

Yes, the operation will be performed under water primarily to keep the solid fines in the water phase. We believe that we would have better chance of removing the fines from the water than from the air.

"Does your feed mechanism feed one at a time, or the whole assembly?"

Response - L. L. Zahn:

Yes, it will feed the entire assembly.

"And the shearer then cuts across individual rods and gaps between rods?"

Response - L. L. Zahn:

That is right. It takes the whole assembly in one shear operation. It will cut through the entire assembly in one drop.

"According to the canister, I was not clear. I think the answer to the last question indicated the canisters are expendable as each fuel process goes in the process. Is that correct, or are they returnable?"

Response - L. L. Zahn:

We would hope that they would be returnable. We would wish to store the cask containers within the storage tanks for some period of time, but we visualize no damage to the containers while in the storage tanks except possibly by contamination. We would plan to return empty cask containers to the shipper within the cask. We would encourage the reactor operator to construct these cask containers of stainless steel in order that they might be readily decontaminated.

"Considering the case of a fuel element which is shipped in and upon which no mechanical process is performed, what is the cask container constructed of and how would it be returned?"

Response - L. L. Zahn:

The cask container should be constructed of stainless steel to facilitate decontamination, and it, or an identical container, would be returned within the empty cask. The cask container would not necessarily totally enclose and contain the fuel element but might be an open bucket as long as its design would permit us to handle the fuel element with the remote crane without the possibility of dropping the assembly or any fragments from it onto the canyon deck.

"I think it was said that the Operations Offices will carry out the negotiations with the individual reactor operators with respect to processing their fuels. Is this correct? Does this apply to all phases of the contract, or just the mechanical operational phases?"

Response - F. P. Baranowski:

The entire processing agreement is one package and includes: the processing charges, the receiving schedule for the cask, the return schedule, the establishment of the processing batch, the termination clauses, etc.

ICPP PLANS FOR PROCESSING IRRADIATED FUELS FROM RESEARCH, TEST, AND POWER REACTORS

by

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Facilities of the Idaho Chemical Processing Plant are available for processing a wide variety of fuels from research, test, and power reactors, particularly those containing highly enriched uranium. These facilities include a storage basin, batch and continuous dissolving equipment for aluminum fuels, dissolvers for zirconium and stainless steel fuels, Hexone and tributyl phosphate extraction columns, uranyl nitrate product bottling means, waste storage vessels, and necessary auxiliary facilities. Plant equipment has been successfully operated for from two to six years on a variety of fuel types and will be modified only slightly for purposes of the interim processing program. Consequently, in contrast to the discussions of other sites involved in the program, this discussion will largely be concerned with existing facilities and how they are adapted to the fuels anticipated. It is proposed to summarize the nature of the fuels expected, the equipment available, and the processes to be used. Later speakers will describe receiving, transfer, and fuel storage means; detailed applications of the processes to be used; and the means for and precision of uranium input measurements.

I. SUMMARY OF ANTICIPATED FUELS

It is contemplated that fuels from at least 40 different reactors will be processed in ICPP facilities. Since firm data cannot be obtained for many of these reactors, which are in various stages of planning, design, and completion, and since other reactors will undoubtedly be added to the list, this is only an order-of-magnitude estimate.

In reviewing the various fuels, data of primary significance

to uranium recovery are: (1) the principal structural material which determines the acid required, (2) shape, weight, and overall dimensions, which affect handling means and dissolving vessel suitability, and (3) uranium content, which is reflected in process capacity.

A. Plate-Type Aluminum Fuels

More than half of the 40 reactors utilize the familiar MTR-type fuel assembly, consisting of 10 to 19 flat or curved plates of aluminum-clad aluminum-uranium alloy (13 to 26 percent uranium) contained in a box-type aluminum assembly as shown in Figure 1. Although there are many minor variations in these fuels, and the length of the assembly as placed in the reactor may considerably exceed the relatively standard 24-5/8 inch plate, most of these fuels can be reduced to a length of a little over 2 feet by removal of end boxes which contain no fuel. Such removal of excess aluminum is highly desirable from the standpoint of the fuel processor since each kilogram of aluminum dissolved for processing otherwise requires a volume of storage space for highly active waste costing about \$15. The normal assembly with ends removed weighs about 4 kilograms and may initially contain 140 - 220 grams of highly enriched uranium. Most of the reactors in this group are of a research type and discharge at most a few kilograms of uranium annually.

There are a few reactors utilizing similar, but longer, fuel assemblies; for example, the ETR and the GETR fuel plates are 37 inches long, the cut assemblies are correspondingly longer, and initially contain 270 - 400 grams of enriched uranium. Sandia reactor fuel is intermediate in length. The SL-1 reactor, formerly designated as the Argonne Low Power Reactor (ALPR), utilized a fuel which is another sort of variation from the MTR type. The 3.9 inch square assembly contains plates 28 inches long fabricated of an aluminum alloy containing one percent nickel. Each assembly weighs about 7 kilograms prior to end box removal and initially contains 320 grams of uranium.

B. Tubular and Other Special Aluminum Alloy Fuel Shapes

There are three research and test reactor aluminum fuels which are tubular in shape and of varying length. The elements are composed of concentric tubes. Data for these fuels are summarized in Table 1. The Argonne CP-5 reactor will use 2 or 3, 27- to 31-inch, concentric tubes with an outer diameter of 2.6 or 3 inches. The assembly initially contains 110 or 130 grams of uranium and up to 1.54 kilograms aluminum. The Westinghouse Test Reactor utilizes a similar but longer assembly of 3 concentric tubes, the largest of which is 2.5 inches in diameter with an overall length of 44 inches. The inner tubes have outside diameters of 2.1 and 1.6 inches.

The assembly initially contains 220 grams of uranium and 4.4 kilograms of aluminum. The last of the tubular reactor fuels being considered is that from the Belgian Test Reactor (BR-2), which is a 6-tube assembly of still greater length (48 inches). The disassembly and handling of concentric tube assemblies, and the great length of some, will introduce some unique problems.

The Brookhaven graphite reactor uses a 24-inch-long fuel element which is not a tube but consists of three plates bent and welded in a star shape, with re-curved fins extending outward for an effective diameter of 2.5 inches. Each element contains initially 15 grams of uranium and 210 of aluminum. Another unusual fuel, of only minor significance because of low power and infrequent reactor discharge, is that derived from the Knolls Laboratory Thermal Test Reactor (TTR). This consists of 28 3-inch diameter thin disks of aluminum-clad uranium-aluminum alloy assembled on an 18-inch spindle. Processing of enriched aluminum alloy fuel from the Chalk River NRX reactor is also considered. This consists of aluminum-clad rods 8 inches long by 1-1/4 inches in diameter.

C. Zirconium Fuel Compositions

The significant highly enriched zirconium fuel is that utilized as core seed elements in the Pressurized Water Reactor (PWR). The elements presently in use are similar in shape to MTR fuel, but much larger and composed principally of Zircaloy-2. The assembly consists of four plate-type subassemblies grouped to form a box 5.5 inches on a side and about 6 feet long as shown in Figure 2 with end sections removed. The plates are composed of an alloy of Zircaloy-2 consisting of 6.3 percent uranium which is clad with Zircaloy-2. All structural members are Zircaloy-2. The assembly is quite massive and initially contains 2.5 kilograms of highly enriched uranium and 127 kilograms of Zircaloy.

D. Stainless Steel Fuel Compositions

The highly enriched uranium-stainless steel fuel compositions generally consist of a matrix of a sintered mixture of stainless steel and uranium dioxide powders, clad with stainless steel and formed into a suitable structure. Of the five fuels of present concern, four are of plate-type construction and one is tubular with characteristics summarized in Table 2.

The Organic Moderated Reactor Experiment (OMRE) fuel, the first core of which has already been partially processed, is a flat-plate MTR-type assembly utilizing Type 304L stainless with 2 percent silicon in the fuel matrix, and forms a box 2.8 x 2.9 inches in cross-section and 37 inches long with ends removed. The SM-1 core (formerly known as the Army Package Power Reactor, APPR-1)

AI-CLAD, AI-U ALLOY
10-19 PLATES
0.05-0.06" THICK

REACTORS USING SIMILAR ELEMENTS

MTR	RER	TSR	ASTR	SPERT
ORR	BRR	MRR	LPTR	CURTIS-WR.
OWR	NRR	LITR	MITR	PENN STATE
IRL	BSR	GTR	NETR	UNIV. MICH.

ELEMENTS WITH LONGER PLATES: ETR, GETR, SERF

Figure 1

Figure 2

is quite similar except that the trimmed assemblies contain about 2/3 as much uranium and are considerably lighter. The Vallecitos Boiling Water Reactor Assemblies (VBWR) are again similar but longer (45 inches) than those from the OMRE, and contain still less uranium and stainless steel. The SPERT III assemblies contain plates of about the length of those from the VBWR but are intermediate in uranium and stainless steel content between those from the OMRE and the SM-1.

The proposed superheater core for the Northern States Power Reactor (CRBR) is of a different nature. Although the boiling section of the reactor for this facility will use slightly enriched uranium, one version of the proposed superheater consists of assemblies of 2 concentric stainless steel-clad tubes with a matrix containing highly enriched uranium as UO_2 . The tubes are 6 feet long and the larger one has an O.D. of 0.71 inches. Each assembly (there are to be 429 in the core) initially contains 79 grams of UO_2 and 255 grams of stainless steel.

It may be seen that the variety of fuel elements and materials is considerable. Minor equipment modifications are planned to facilitate handling of bulky fuels by removal of excess metal, or by size reduction. The available processes and facilities will next be reviewed.

II. PROCESSES UTILIZED AT THE ICPP

The ICPP is a flexible, multipurpose facility designed to process enriched uranium reactor fuels. It is multipurpose in that, although initially designed to process aluminum alloy fuels in a batch dissolving-three Hexone cycle extraction system, equipment was later added to dissolve and perform first cycle tributyl phosphate (TBP) extraction of zirconium and stainless steel fuel compositions, the product of which is further decontaminated in the Hexone extraction system provided for aluminum fuels. A small dissolver was also provided for essentially unalloyed highly enriched uranium, and was used for the first core of the Experimental Breeder Reactor (EBR-1). In another modification, equipment was added for continuous dissolution and first cycle TBP extraction of aluminum fuels. Further decontamination is again accomplished in the Hexone system. For most fuels and operating conditions, the continuous dissolution system can be operated at greater efficiency than the batch system. The plant is flexible in that, by interconnection of the multiplicity of dissolving and extraction equipment available, as well as by use of the special means for storage and handling of fuels, it is peculiarly suited to handling a wide variety of special shapes and compositions.

It may be noted that, even though the plant was designed for high enrichment uranium fuels, it is only limited in handling lower enrichment fuels, for which separate plutonium recovery may

be required, by the absence of a simple system of similar type to those now in use for plutonium partition and further decontamination.

It is generally characteristic of highly enriched uranium fuel processing that the metals used for fuel cladding and core matrix mixtures or alloys--aluminum, zirconium or stainless steels--determine the dissolving reagent requirements and initial extraction process throughput. This is so because present processes involve essentially complete dissolution of the fuel elements. Thus, the various processes are based on solubility limitations of the fuel diluent metals, whose solutions are carried through into the waste streams. For a given total metal throughput, uranium content and throughput can generally vary within wide limits. Later processing steps, in which separated uranium is further decontaminated, can generally be conducted in much smaller equipment. The processes to be used for aluminum, zirconium, and stainless steel fuels are summarized in Table 3.

A. Aluminum Alloy Process

Uranium is recovered from aluminum fuel compositions; i.e., of the MTR type, by dissolving in nitric acid to which a small amount of mercuric nitrate is added to accelerate dissolving. After adjustment of acidity uranium is extracted from the aluminum nitrate solution by contacting with either Hexone or a few percent of tributyl phosphate in a kerosene-type solvent. The removal of fission products from the TBP-uranium solution is augmented by scrubbing it with fresh aluminum nitrate. The uranium is then stripped back into a water solution by contacting with very dilute nitric acid. After concentration of the latter solution by evaporation of water, the uranium is mixed with additional fresh aluminum nitrate solution and further decontaminated by two extraction cycles in which Hexone is used as the solvent. The product of all processes is a concentrated uranyl nitrate solution. Any plutonium present is rejected to waste streams by the addition of a reducing agent in one of the extraction cycles.

B. Zirconium Fuel Process

Hydrofluoric acid is used to dissolve zirconium or Zircaloy compositions containing overall up to about 2 per cent of uranium. The insolubility of greater amounts of uranium tetrafluoride in the resulting zirconium fluoride solution affects the processing of fuels containing a larger proportion of uranium, although small quantities of oxidizing agents may be added to convert uranium to the more soluble uranyl form. The tin contained in Zircaloy requires the addition of a small amount of nitric acid at the end of the element dissolving to place it in solution. Since uranium cannot be extracted directly from the fluoride solution, the latter is mixed with aluminum nitrate solution to complex the fluoride, and uranium is

Table 1

Tubular Aluminum Fuels

<u>Reactor</u>	<u>No. Tubes</u>	<u>Maximum Diameter (inches)</u>	<u>Length (inches)</u>	<u>g. U</u>	<u>Kg. Al</u>
CP-5	2 or 3	2.6 - 3.0	27 - 31	110-130	1.5
WTR	3	2.5	44	210	4.4
BR-2	6	3.0	48	---	---

Table 2

Stainless Steel Fuels

<u>Reactor</u>	<u>Type</u>	<u>Cross Section</u>	<u>Length</u>	<u>g. UO₂</u>	<u>Kg. SS</u>
OMRE	Plate	2.8" x 2.9"	37"	1000	8.3
SM-1	Plate	2.8" x 2.9"	33"	630	4.6
VBWR	Plate	3.0" x 3.0"	45"	220-230	> 2.5
SPERT	Plate	3.0" x 3.0"	~ 40"	780	9.0
CRBR-SH	Tube	0.71" Dia.	72"	79	0.3

Table 3

ICPP FUEL PROCESSES

<u>Reagent for</u>	<u>Aluminum Fuel</u>	<u>Zirconium Fuel</u>	<u>Stainless Steel Fuel</u>
Dissolving	Nitric Acid Mercuric Nitrate	Hydrofluoric Acid - Nitric Acid	Sulfuric Acid - Nitric Acid
Complexing -- Salting	Aluminum Nitrate (from fuel)	Aluminum Nitrate	Nitric Acid
First Ext'n	TBP or Hexone	TBP	TBP
Final Ext'n	Hexone	Hexone	Hexone

recovered from the resultant solution by extraction with 10 percent tributyl phosphate in hydrocarbon mixture. Processing steps thereafter are essentially the same as used for aluminum fuels.

C. Stainless Steel Fuel Process

In order to dissolve stainless steel fuel compositions completely, two reagents are necessary. The stainless steel is dissolved in sulfuric acid, following which the uranium oxide residue is dissolved by the further addition of nitric acid to the stainless steel sulfate solution. Additional nitric acid is added to force the uranium into the extraction reagent, which again is 10 percent tributyl phosphate in a hydrocarbon solution. Again, the uranium solution is further processed in the same manner as that derived from aluminum and zirconium fuels.

III. FACILITIES OF THE ICPP

A. Plant Layout

A plot plan of the Idaho Chemical Processing Plant is shown in Figure 3. The area contains 5 main buildings plus the underground tank farm for the storage of radioactive wastes. The principal buildings are the main process building and adjacent laboratory, a fuel storage basin, a waste processing building, and a utilities service building.

The incoming fuel storage building is located 1/3 mile south of the processing building on a railroad spur and houses three basins (over 9000 square feet total basin area) for the storage of fuel elements in 20 feet of water, and three transfer basins for the loading and unloading of fuel element carriers.

The waste disposal building houses a low-activity liquid waste evaporator and exhaust fans and filters for process building ventilation. A 250-foot stack for discharge of waste gases and ventilation air is located next to the waste building.

The laboratory and administration building adjoins the process building on the north. This building contains offices, low-level analytical and process development laboratories, maintenance shop, and other service facilities.

The utilities building, which houses the steam plant, electrical equipment, heating and ventilating equipment, and other services, is located just north of the laboratory building.

The process building, which houses the bulk of the process equipment, is constructed of reinforced concrete and is approximately 240 feet long, 100 feet wide, and a maximum of 60 feet deep. These

Figure 3

dimensions exclude a steel-and-transite building which covers the cell area and houses the chemical makeup and fuel charging area. The active process equipment is contained within 24 cells, each typically about 20 feet square and 28 feet deep, which are shielded with up to 5 feet of concrete. An elaborate and highly flexible remote analytical facility for direct analysis of highly radioactive process streams is attached to the process building.

The process building contains two rows of cells, separated by operating, service line, and access corridors, with sampling and vent corridors, at either side.

Tanks used for storage of radioactive wastes are located to the east of the plant and are typically large stainless steel vessels located in underground concrete vaults with earth cover. The waste tank farm contains 13 vessels, 9 with a capacity of about 300,000 gallons each, and 4 which hold 30,000 gallons each. The latter are used only for first cycle wastes from zirconium and stainless steel processing. Six of the 300,000-gallon tanks are equipped with cooling coils in order that they may be used for the high activity wastes from first cycle processing of aluminum fuels, as the rate of heat generation from decay of fission products is such as to require cooling to minimize corrosion. Almost a million gallons of such wastes are now in storage. The remaining 300,000-gallon tanks are not cooled and are used for wastes of intermediate activity, principally as obtained from second and third extraction cycles.

B. Design Features

Because much equipment, such as is required for dissolving and first cycle extraction, rapidly becomes very highly contaminated with radioactive materials, the problem of equipment maintenance and repair requires special consideration. At the ICPP special cranes and equipment assembly means to permit maintenance efforts to be conducted remotely have not been provided; consequently, it is necessary to decontaminate equipment which is defective in order that personnel may have access to it to make repairs, adjustments, or modifications.

The process equipment is designed with sufficient capacity to allow periodic shutdown for maintenance operations and spares are provided for essential units. The equipment is of simple mechanical design for easy decontamination and repairs, and contains a minimum of moving parts. Solution addition funnels, circulating jets, and heating means are provided to facilitate decontamination. Insofar as practical, equipment is segregated by activity level to permit decontamination simplifications for equipment less likely to be contaminated.

The workability of this philosophy is attested to by the fact that all process cells have been decontaminated sufficiently for personnel entry and maintenance from one to several times. This type of design has resulted in substantial construction cost savings as compared to remote maintenance plants. Design for direct maintenance allows a maximum of process equipment to be placed in each cell, as no provision need be made for removal by remote methods.

In the processing of highly enriched uranium at high concentrations, design must prevent the accumulation of more than certain quantities or concentrations in various parts of the process to eliminate the possibility of initiating nuclear chain reactions. In the ICPP, each process vessel is made safe by (a) limiting the mass of material allowed to enter the vessel (for example, the charge to a dissolver), (b) providing a vessel geometry such that critical conditions can never be achieved (for example, by limiting the diameter of uranium storage vessels), or (c) by defining process conditions such that the concentration of fissionable material cannot enter the range where a chain reaction is possible (for example, the solubility of aluminum nitrate and the ratio of uranium-to-aluminum in the fuel limit the concentration of uranium which can be obtained by dissolving such a fuel).

C. Processing Sequence and Interrelationships

Process equipment for carrying out the various operations required for uranium recovery is grouped in the cells of the main process building as shown in Figure 4. For example, two cells each contain two batch dissolvers and associated feed makeup vessels for treatment of aluminum fuels; the next pair of cells contains a batch dissolver for zirconium fuel, a batch dissolver for stainless steel fuel, adjustment and hold vessels, and columns for first cycle extraction with tributyl phosphate, while a third pair of cells contains two continuous dissolvers for aluminum fuels and a higher capacity tributyl phosphate first cycle extraction system. These three cell groups along with a cell for first cycle Hexone extraction contain essentially parallel "headend" dissolving-extraction systems which provide concentrated and partially decontaminated uranyl nitrate solution for feed to the second and third cycle Hexone extraction cells located on the opposite side of the plant (note: the initial extraction of batch-dissolved uranium may be accomplished by either Hexone or TBP).

The process flow pattern is indicated by the heavy lines and arrows on the slide, with some of the possible alternate paths being shown by dashed lines. Flexibility for sequential or simultaneous operation of the several headends and the final decontamination system is provided by a large feed storage cell, containing several banks of critically safe vessels, wherein concentrated solutions of fissionable material from intermediate processing steps may be

Figure 4

safely accumulated.

Other cells in the process building contain equipment for concentration of wastes, for recovery and storage of used Hexone solvent (TBP solvent treatment for re-use is accomplished in the extraction cells), and for preparing uranium-bearing waste streams or other off-specification material for re-work. Other uses of the available plant equipment are possible with minor piping changes.

IV. SUMMARY

The variety of highly enriched uranium fuels, which consist primarily of aluminum, zirconium, or stainless steel, and are of various shapes and sizes, proposed for processing at the ICPP has been indicated. The applicable facilities and processes have been outlined to indicate the flexibility of this plant for handling all presently anticipated fuels in this category. Subsequent discussions will describe in detail the receiving and storage facilities and procedures, the applications of the processes to typical fuels, and methods of accounting for incoming material.

ICPP FACILITIES FOR RECEIVING,
STORAGE AND MECHANICAL TREATMENT

by

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Presented by

C. B. Leek

The Idaho Chemical Processing Plant is equipped to handle a large variety of irradiated fuels. The fuels, as received, have a minimum of 90 days cooling and a minimum of 120 days cooling before being sent to process. We are equipped to handle casks weighing up to 75 tons by either rail or motor freight. In all cases, fuel casks must be compatible with our unloading and underwater handling equipment. Some of the more specific limitations on the size of casks will be discussed later.

Unloading and storage of irradiated fuel is carried out in the SS Storage Building. This building was built in 1950-51 concurrent with the construction of the main Chemical Processing Plant. The facility was originally intended for storage of enriched fuel from the Hanford Site and enriched fuel from the NRTS reactors such as the Materials Testing Reactor. Since that time, a large variety of fuels has been handled from reactor sites throughout the country.

A simple layout of the building is shown in Figure 1. The building is located about 1/3 mile south of the main processing plant and consists of a crane bay 200 feet long by 29 feet wide and 33 feet high serviced by a 15 ton crane. A canal 200 feet long, 7 feet wide and 21 feet deep runs parallel to the crane bay. Two storage basins each 40 feet by 60 feet by 21 feet extend at right angles at the middle and north sections of the canal. Another storage basin about 40 feet by 80 feet by 21 feet was constructed in 1957-59 at the southeast edge of the canal and will be described later. Loading and transfer pits about 7 feet by 25 feet extend

Fig. 1—S. S. storage building.

from the canal opposite the storage basins and adjacent to the crane bay. The below grade and surface portions of the building are reinforced concrete. The upper structure is structural steel with corrugated asbestos siding on the outside walls and roof and flat asbestos on the inside with fiberglass between. Heating and ventilating equipment is housed in 20 foot by 16 foot annexes on the east ends of the storage basins. Heat was originally provided by oil fired air heaters which have been converted to steam air heaters. The basins and canal contain about 1,500,000 gallons of water. The water is treated with 250 p.p.m. of sodium nitrate to inhibit corrosion of underwater structure. Chlorine is added to .1 - .2 ppm residual chlorine to control microorganism and algae growth. Water is recirculated at the rate of 400 gallons per minute through two diatomaceous earth coated filters which maintain the required clarity of the water.

Infrequently the basin water has become "cloudy" due to high concentration of various microorganisms. Apparently, when the water conditions are optimum, these organisms reproduce rapidly causing cloudiness, then the water becomes overly populated with them causing conditions unfavorable to their continued growth and reproduction and they die and are filtered out. At these times, the basin water is "shock treated" with chlorine which brings the water chlorine residual up to about one ppm for a short period of time. The sodium nitrate corrosion treatment is stopped temporarily as it has been determined that at least some of the organisms feed on the nitrate ion. The organic slimes filtered from the water tend to plug the filters and require more frequent backwash and eventual replacement of the filter stones. In general, the water treatment has been satisfactory as the basins have been in service for nearly eight years without being drained and cleaned with only a thin layer 1/8 to 1/4 inch thick of accumulated dirt on the floor of the basin. An underwater vacuum cleaner designed to remove this dirt is currently being tested.

Buildup of radioactivity in the storage basin has not been a major problem. Activity of the water is about 2.5×10^2 c/m/ml and rises to about 5×10^2 c/m/ml when unclad alloy type fuel is exposed to the water. Storage of large amounts of unclad fuel for long periods of time would undoubtedly cause the water activity to rise far above these values.

The storage basins are each divided into 29 channels by concrete spacers at the bottom and pier supported concrete spacers at the top. The spacers are 2 foot high by 1 foot wide on 2-foot centers. Buckets of fuel in storage are suspended in the channels between the spacers by bucket yokes which ride on overhead mono-rails. The basins and the canal are covered with 1 inch steel grating with 1 1/2 inch slots beneath the monorails to provide passage for the bucket yokes. These basins provide storage for

about 1,000 buckets of fuel.

A typical yoke and storage bucket is shown in Figure 2. The bucket yokes and suspended buckets ride overhead monorails. Turntables are provided at each intersection of monorails for changing direction or transfer to another rail. Two monorails extend the length of the canal and provide adequate "juggling" and switching space such that any bucket in any storage position can be transferred to the loading pits or vice versa. Bumpers at the top of the bucket yoke and immediately above the buckets maintain a 2 foot center-to-center spacing in this dimension while the concrete spacers in the bottom of the basins guarantee the same 2 foot center-to-center spacing in the other dimension. The yokes are galvanized carbon steel. The storage buckets are usually fabricated from aluminum plate and are of varying sizes with the maximum size of 11 inches by 15 inches by 33 inches high. Black iron buckets have been used, but corrosion soon made it necessary to replace them. It is planned to standardize on aluminum buckets in the future. The buckets contain various type spacers depending on the type of fuel stored.

The layout of the transfer and loading pits is shown in Figure 3. The two identical loading pits 6 by 9 by 26 feet deep are on each side of a central transfer pit that is 6 feet by 7 feet by 21 feet. Cask guide rails extend to the bottom of the loading pits and limit the size of the cask to 4 feet wide by 5 feet long and up to about 8 feet high. As casks are received, any cask lid bolts or locking bars are removed and the cask picked up with the 15 ton crane by two free-swinging hooks and lowered into one of the loading pits. As the cask is lowered, the cask lid outrigger beams engage two I beams about 12 feet under the surface of the water. The cask lid is retained on these beams as the cask is lowered to the bottom of the pit. The uncovered cask is then moved laterally from under the suspended lid toward the transfer pit. A section of the monorail over the loading pit is suspended from a hydraulic cylinder so that a bucket yoke or hook can be lowered into the cask and a full bucket of elements removed with the hydraulic lift. The elements are moved into the central transfer pit, identified and transferred with tongs into a storage bucket. In some instances, the shipping bucket can also be used as a storage bucket eliminating extra handling of the elements. As the bucket is moved from the transfer pit to one of the storage basins, it crosses a "floating" section of the monorail which is connected to a 100 kg Howe Mechanic-print Scale. The loaded bucket is weighed to the nearest 0.1 kg and the weight punched on a SS Accountability Receiving Form. In the case of a large number of small slugs in one bucket, the scale sensitivity is adequate to detect a missing slug.

A typical fuel handling tong is shown in Figure 4. The tongs are about 24 feet long and are equipped with a float chamber about

Fig. 2—MTR bucket, bucket yoke, and trolley.

Figure 3

Figure 4

4 feet long to provide buoyancy. The jaws are spring closed and are opened by squeezing the handles together. A number of different type jaws can be installed to handle the various sized elements.

A new basin and hot cell called the Fuel Element Cutting Facility was built in 1957-58 at the southeast corner of the original building. The new building is about 137 feet by 90 feet. It contains a crane bay 137 feet by 40 feet by 40 feet high serviced by both a 75 ton crane and a 15 ton crane. A railroad spur track runs through the crane bay. An open storage basin about 40 feet by 80 feet and 21 feet deep is serviced by an overhead transfer crane of 1 ton capacity which has a riding cab for the operator and can traverse the whole basin area. Filtered water is supplied to the basin by the existing water system and overflows a weir into the canal of the main storage building. The hot cell is 31 feet long, 10 feet wide and 14 feet high with 5 foot concrete walls and 4 conning glass viewing windows. A tunnel runs beneath the hot cell for removing the cut fuel elements in 15 ton chargers. Fuel can be received by truck or railroad car in casks weighing up to 75 tons. Cask tiedown studs and lid bolts are removed with an air operated impact wrench and the cask picked up with the 75 ton crane and lowered into the transfer basin. At about 11 feet under the water the cask lid outriggers engage a holding beam and lugs which suspend the cask lid at this elevation while the cask is lowered to the bottom of the basin and moved laterally north from beneath the lid. The 75 ton crane is moved clear of the cask and a jib track for the 1 ton transfer crane is lowered over the cask. The transfer crane is used to remove the loaded fuel magazines or containers from the cask and to place them in storage racks in the basin. The transfer crane is also used to deliver loaded magazines to a magazine unloading table on the floor of the basin at the rear of the hot cell. Two parallel endless chains with fingers run from the magazine unloading table up through a submerged slot in the rear of the cell and deliver the fuel elements into a feed trough in the cell. This system can deliver up to 16 feet long elements into the cell. The cell contains hydraulically-operated equipment which is capable of altering the shape of certain simple elements and cutting them into lengths compatible with existing dissolution equipment in the processing plant. Hydraulic power to the cell equipment is transmitted by concentric push and pull rods which extend through the cell wall to a 3,000 psi hydraulic unit mounted outside the cell. The cell and the tunnel beneath the cell are equipped with mechanical devices to remove buckets of cut fuel from the cell into 15-ton chargers. All of the remote operations are controlled either manually or automatically from control consoles located under the viewing windows at the south face of the cell. A number of K plug ports is provided through the face of the cell for installation of Argonne Model 8 Master Slave Manipulators and the cell is equipped with a bridge mounted General Mills Manipulator which can traverse the whole cell. Cell ventilation is provided

by a 1,000 scfm blower which pulls air from the cell through a roughing and absolute filter and exhausts the air to the atmosphere through a 6 inch diameter stack which extends about 10 feet above the building roof. About 1 inch H₂O vacuum is maintained on the cell. An incell vacuum system for control of dust and particulate was installed. The vacuum picks up under the cutting equipment and chute passes air and particles through a cyclone and a filter to a 300 scfm blower mounted in the tunnel below the cell which exhausts the air back into the cell. The cell is also equipped with an extensive water and steam spray system. Cell floor drains drain to a hot waste tank located in a small separate building. Solutions can be transferred from this hot waste tank to the processing plant waste handling systems. Activity levels when the cell is in operation are in the 10^6 - 10^7 R/hr range.

If the fuel processed in this facility shatters during cutting, the cell may be littered with particles of fuel fragments. The shattering of the fuel poses severe cell decontamination problems for maintenance of incell equipment which is inevitable for equipment in 24 hr/day use for long periods of time. The General Mills Manipulator has been an extremely valuable tool for removal of the litter of fuel fragments and dust. Maintenance on the General Mills itself has been accomplished without incell decontamination by removing it from the cell and repairing it outside.

Figure 5 shows a shielded box constructed to permit removal of the General Mills Manipulator and other simple incell maintenance without cell decontamination. The box has four-inch lead walls, a six-inch thick viewing window and a hinged rear door for access. The box is provided with forced air ventilation and a communication system. It has a central manipulator port and two arm ports from which the shielding plugs can be removed from inside. The box with a man inside is lowered into the cell with the 15 ton crane. A number of simple incell maintenance jobs have been accomplished with the box, some with the tong and some directly through the armholes taking advantage of the relatively high permissible exposure for hands.

It is planned to add an underwater saw for end piece cutting and other simple dismantling equipment to the Fuel Element Cutting Facility basin in the near future. There are no immediate plans to section research, test and power reactor fuel elements in the basin by cutting into the fuel meat and thus exposing unclad fuel to the basin water. If such a problem comes up, modification of the hot cell equipment to handle a variety of fuels might be the most satisfactory solution.

Each type of fuel that is to be handled by this facility is reviewed by a Safeguard Committee. Criticality limitations for the fuel are received from the shipper and these limitations are

Figure 5

checked by appropriate criticality calculations. The number of elements per bucket and their geometry are specified. The criticality considerations of the fuel storage are guaranteed by the physical size and shape of the buckets and bucket spacers or by administrative control of the number of elements per bucket or both. To date, limiting the number of elements per bucket for criticality has been satisfactory; however, it is anticipated that fuel of higher uranium content which will be received in the future may require the use of neutron poisoned buckets for efficient utilization of storage space. All fuel received in storage, transferred from one storage position to another or shipped out of the storage area is accurately identified and recorded on transfer forms. In addition to the operational records that are kept on fuel inventory, a SS Accountability group maintains a complete and separate record of fuel inventory.

Most fuel transfers within the National Reactor Testing Station and all fuel transfers between the storage building and the processing plant are made by 15 ton capacity Gerlinger straddle carriers thus generally limiting the on-site carrier cask design. Many of the on-site fuel carriers also serve as fuel chargers. A typical on-site charger-carrier is shown in Figure 6. Charger-carriers of this type with either a 10 inch square by 49 inch deep or 11 inch square by 27 inch deep center cavity are currently in use at the ICPP. These have movable motor-driven bottom drawers to discharge the elements into a dissolver. They are constructed of stainless steel with 8 to 12 inches of lead shielding. The lead filled lid is equipped with outriggers to suspend the lid in the loading pits. The fuel cavities can be equipped with a variety of buckets or spacers depending upon the particular fuel being handled. Carriers used only for shipping have a solid bottom. Rotary chargers are available for charging elements less than 21 inches in length. These chargers have the standard lead filled removable top with outrigger, a rotating drum in the middle and a shielding slide drawer on the bottom. A storage bucket full of fuel can be placed in the drum without disturbing the fuel. The top is put on and the charger is transported to the process building. The slide drawer is opened and the drum and bucket can then be rotated to discharge the fuel into a dissolver. The whole charging sequence is carried out without handling the individual elements. This greatly reduces the work required to handle small fuel elements.

Shipping casks for fuel from other sites are generally designed for a specific fuel or a specific group of fuels such as the MTR type fuels. Either the reactor operator or his shipper provides the shipping cask. Large casks such as the 75 ton railway cask minimize unit freight rates if the shipping program is large enough to sustain the high capital investment for such a cask. Most casks are stainless steel with lead shielding. The

Figure 6

cost of decontaminating black iron may soon more than offset savings made by using this material. A shipping cask must be able to withstand a reasonable amount of rough treatment without damage. Geometric optimization in some of the newer transfer casks has materially reduced the unit shipping weight. Bureau of Explosives' approval of all casks used in inter-site shipments is mandatory.

Summary

The ICPP facilities for unloading, storage and charging irradiated fuel elements are flexible enough to handle a large variety of fuels. However, if the fuel is to be handled efficiently and economically, there must be close liaison between the shipper and the plant.

Casks up to 75 tons in weight may be received by rail or motor freight. Whether large or small, a shipping cask must be compatible with the available unloading and underwater handling equipment if the fuel is to be handled. The physical limitations for this equipment is readily available at ICPP.

Complete data including detailed composition of the elements, geometric configuration, removable non-fuel bearing parts and criticality limitations including any neutron poison present in the fuel cask must be received by ICPP well in advance of any shipment. Inadequate or improper information can result in expensive special handling or return of the shipment. Fuel must have a minimum of 90 days cooling before it will be accepted for storage at ICPP. End plate cutting and simple dismantling can be carried out at ICPP, but complex mechanical operations can probably best be carried out at the reactor site.

ICPP DISSOLUTION, EXTRACTION,
AND WASTE TREATMENT PROCESSES AND FACILITIES

by

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Dr. Stevenson's paper discussed plans for processing Research, Test, and Power Reactor fuels at the ICPP and presented an overall view of processes and facilities. This paper will describe the processes and facilities in greater detail, including chemical flowsheets and schematics of the various processes, and will in a general way give limitations that exist for processing various fuels as to fuel size, shape, composition and weight.

It should be emphasized that the fuel processing plant must have complete details on the fuel to be processed, including fuel drawings, and fabrication methods and details. To have only the overall weight and dimensions of a fuel, with plate thickness and percentage uranium and alloying-cladding components is not enough. The fuel questionnaires even if filled out carefully and completely are inadequate; references on methods of fabrication should be furnished. It may not be obvious, but the presence of any amount of extraneous material is significant; thermocouples, for example, are frequently insoluble in the dissolving medium and cannot be tolerated. Silicon, added to improve the fabrication characteristics of a material, can cause the plugging of equipment or prevent the proper operation of extraction columns. No detail is too insignificant to be of concern to the processing plant, and especially if unexpected trouble develops after a processing run has been started.

I. ALUMINUM FUEL REPROCESSING

A. Continuous Head-End

The continuous dissolution and TBP first cycle equipment for aluminum fuel will be used whenever the quantity, size, and shape of the fuel permit its use. It has a higher capacity than the batch system, and requires fewer operators, and laboratory analyses, and less chemicals per unit of fuel.

1. Flow Diagrams and Equipment

As mentioned in Dr. Stevenson's paper, the fuel is dissolved in nitric acid, using mercuric nitrate as a catalyst. Figure 1 shows a schematic of the dissolving system. There are two such dissolvers and filters. Fuel is dropped into the charging cave from a charger. It is picked up with a master-slave manipulator and dropped into the appropriate dissolver. The manipulator has a capacity of 15 to 20 pounds and the maximum length that can be handled is about 38 inches, the length of an ETR element after removal of the end boxes. ETR elements have not been processed through this equipment, although it has been modified to handle them. The "slug chute" passing through the cooling coil is a sleeve having a 5.83-inch inside diameter; obviously, elements having a larger corresponding size than this cannot be handled.

Overall length of the dissolver is 26 feet; the lower section, up to the product overflow, is 16 feet long and 7 1/2 inches inside diameter. As indicated in the figure, the acid-catalyst mixture is introduced at the bottom and passes up around the dissolving metal. The filter is a 100-mesh screen. The input measurement is made in the feed tank; two of them are used alternately. One is agitated and sampled while the other is being filled. No feed adjustment is required; after the input measurement has been completed, the material is transferred to the run tank, from which it is sent to the columns. The feed tanks are 4-foot diameter by 8-foot high tanks, having a working volume of some 2300 liters.

Figure 2 is a schematic of the TBP extraction system accompanying the continuous dissolver. The A column is a pulsed, sieve plate extraction column. The plate section is 23 feet long with an inside diameter of 10 inches. The scrub (B) column is a pulsed, sieve plate column, 16 feet long by 8 inches inside diameter. The scrub column raffinate contains appreciable uranium; as a consequence, it is combined with the dissolver product and evaporated to the proper salting strength for A column feed. The scrubbed organic phase is fed to the C column, where the uranium is stripped from the organic by water in the absence of salting agent. The C column is also a pulsed, sieve plate column, 18 feet long by 9 inches in diameter. The lower head is geometry-limited as an aid in criticality control, although it is not "infinitely safe".

Fig 1—Continuous aluminum-uranium alloy feed preparation

Fig. 2—Schematic of TBP first cycle for aluminum fuels.

From the strip column, the product is passed through a wash (D) column and steam stripped before concentration in the first cycle product evaporator. The wash column and steam stripper are both designed to remove traces of TBP to prevent the formation of degradation products in the evaporator. The wash column is a packed column, 5 inches in diameter by 10 1/2 feet high and is not pulsed.

The combination of wash column and steam stripper are underdesigned and do not effectively remove TBP and degradation products, as evidenced by the fact that it has been impossible to concentrate the first cycle product to the design concentration of 1.5 molar uranium successfully. The evaporator or pumps feeding the following cycle have consistently plugged; as a consequence the evaporator product concentration specification has been reduced to 0.75 molar.

The second and third cycles of extraction are schematically identical and are illustrated in Figure 3. The columns are packed and are 2 inches in diameter by 30.8 feet (extraction) and 20 feet (strip) long. The A column is a compound column, the feed being introduced about one-fourth of the column length from the top. There are no wash columns or steam strippers associated with the hexone columns. Since there is no aluminum present in the feed, all aluminum for salting in the A column is provided in the scrub stream. The product from the third cycle (uranyl nitrate solution) is bottled and shipped from the plant.

2. Chemical Flowsheets

Table 1 is the chemical flowsheet for processing MTR fuel through the continuous dissolution system, TBP first extraction cycle, and hexone second and third cycles. The 6.3 molar nitric acid dissolving reagent typically contains 0.007 molar mercuric nitrate, although this may be adjusted to control dissolution rate, within limits. Excess oxygen-enriched air is added to the bottom of the dissolvers and converts part of the oxides of nitrogen back to nitric acid; as consequence, acid consumption is 3.25 moles per mole of metal dissolved. Dissolver product is typically 1.6 molar aluminum and somewhat over one molar nitric acid. Dissolver product is combined with the IB column raffinate (IBR) containing 1.0 molar aluminum nitrate; the mixture is evaporated to 1.6 molar aluminum nitrate and sent to the 1A column as feed (IAF). The 1A extractant (IAX) is 3.25% TBP in Amsco 125-90W; the aqueous-to-organic ratio in the A column is 1.36:1.

In addition to fission product decontamination, the B column serves another important function - that of acid removal from the uranium-containing organic stream. If a large portion of the acid were not removed, the first cycle product after evaporation would be excessively acidic, giving increased corrosion rates in the

Fig. 3—Typical hexone extraction cycle.

TABLE 1

CONTINUOUS DISSOLUTION AND EXTRACTION FLOWSHEET FOR MTR ELEMENTS
(30% BURNUP)

FIRST CYCLE

	<u>Flow</u> <u>(a)</u>	<u>Sp.G</u> <u>25°C</u>	<u>HNO₃</u> <u>M</u>	<u>Al(NO₃)₃</u> <u>M</u>	<u>Hg(NO₃)₂</u> <u>M</u>	<u>NH₄NO₃</u> <u>M</u>	<u>URANIUM</u> <u>g/l</u>
Dissol. Reagt.	97.0	1.199	6.3 ^(b)		0.007		
Dissol. Prod.	93.4	1.296	1.3	1.60	0.007		1.69
IAF	100	1.286	1.23	1.60	0.007	0.03	1.62
IAX	73.6	0.77	(in 3.25% TBP)				
IAR	99.2	1.292	1.18	1.61	0.007	0.03	1.6x10 ⁻⁴
IAP	73.6	0.78	0.08	(in 3.25% TBP)			2.20
IBS ^(c)	11.2	1.159		1.0 plus (0.30 M NH ₄ OH)			
IBR	11.2	1.166	0.13	1.0		0.30	0.4
IBP	73.6	0.78	0.013 (in 3.25% TBP)				2.14
ICX	38.8	1.001	0.01				
ICP(IDP)	39.0	1.014	0.034				4.04
ICR	73.6	0.77	(in 3.25% TBP)				2.1x10 ⁻⁴
IDS(IDR)	3.88	0.76	(in AMSCO)				

(a) All flows relative to IAF = 100. For 100 liters of IAF, 4.03 kg of aluminum and 158g of uranium are dissolved.

(b) Assumes oxygen addition for conversion of oxides of nitrogen to HNO₃.

(c) Consists of all available YI and IIIAR adjusted to specifications and recycled, together with fresh IBS as required to make up balance.

(e) Recycled as first cycle scrub (IBS) after adjustment to 1.0M Al (NO₃)₃, 0.30 / 0.06N acid deficiency with NH₄OH.

TABLE 1 (Continued)

CONTINUOUS DISSOLUTION AND EXTRACTION FLOWSHEET FOR MTR ELEMENTS
(30% BURNUP)

SECOND AND THIRD CYCLES

	<u>Flow</u> <u>(a)</u>	<u>Sp.G</u> <u>25°C</u>	<u>HNO₃</u> <u>M</u>	<u>Al(NO₃)₃</u> <u>M</u>	<u>NH₄OH,</u> <u>M</u>	<u>NH₄NO₃</u> <u>M</u>	<u>URANIUM</u> <u>g/l</u>
IIAF	0.970	1.263 ^(d)	1.36				162
IIAX	3.73	0.80					
	(In Hexone)						
IIAS	2.76	1.320		2.0	0.75		
IIAR ^(e)	0.05 M Fe (NH ₄) ₂ (SO ₄) ₂			and 0.10 M HSO ₃ NH ₂			
	3.70	1.242		1.49	0.20	0.36	0.0043
IIAP	0.04 M Fe (NH ₄) ₂ (SO ₄) ₂			and 0.07 M HSO ₃ NH ₂			
	3.77	0.86					41.8
	(In Hexone)						
IIBX	0.994	1.002	0.04				
IIBP	1.05	1.200	0.04				151
IIBR	3.73	0.80					0.0042
	(In Hexone)						
IIIAF	0.446	1.480	0.09				353
IIIAX	1.71	0.80					
	(In Hexone)						
IIIAS	1.27	1.314		2.0	0.30		
IIIAAR ^(e)	1.65	1.245		1.53	0.21	0.02	0.0095
IIIIAP	1.75	0.933					90.6
	(In Hexone)						
IIIBX	0.609	1.002	0.04				
IIIBP	0.661	1.317	0.04				237
IIIBR	1.71	0.80					0.0092
	(In Hexone)						
Final							
Prod.	0.446	1.479	0.06				353

(a) All flows relative to IAF = 100. For 100 liters of IAF, 4.03 kg of aluminum and 158g of uranium are dissolved.

(d) Density at B.P. = 1.200

(e) Recycled as first cycle scrub (IBS) after adjustment to 1.0M Al(NO₃)₃, 0.30 / 0.06N acid deficiency with NH₄OH.

TABLE 1 (Continued)

WASTE CONCENTRATION AND TBP SOLVENT CLEANUP

	IARm	Mixer I	Settler II	Scrub Streams III
Relative Flow	82.1	0.0736	0.0736	0.0736
Density at 25°C	1.350 ^(a)	1.002		
Al(NO ₃) ₃ , <u>M</u>	1.95			
HNO ₃ , <u>N</u>	1.41	0.04		0.04
Na ₂ CO ₃ , <u>M</u>			0.05	
NaNO ₃ , <u>M</u>	0.09			
Hg(NO ₃) ₂ , <u>M</u>	0.008			
NH ₄ NO ₃ , <u>M</u>	0.04			
Uranium, g/l	1.9 x 10 ⁻⁴			
(a) Density at B.P. = 1.302				

KEY TO STREAM DESIGNATIONS

Roman numeral designates cycle (1st, 2nd, 3rd)

First letter designates column within cycle (A, B, C, D)

Second letter designates kind of stream, as follows:

F - feed

X - extractant

S - scrub

R - raffinate

P - product

IARm = IAR after final concentration

evaporator, increased rates of formation of TBP degradation products, and a possible violent oxidation reaction with hexone in the IIA column. Acid removal is improved by adding ammonium hydroxide to the cold scrub stream.

The strip solution (ICX) is slightly acidic, to reduce emulsion difficulties in this column. By virtue of the 0.53:1 aqueous-to-organic ratio in the IC column, the uranium concentration is again increased in the IC column product (ICP).

The flowsheet does not indicate any removal of TBP in the Amsco wash used in the ID column (ICP-IDP); the quantity involved is quite small. As mentioned previously, the first cycle product after evaporation (IIAF) is usually maintained at about 0.75 molar uranium. Acidity is significant, being normally in the range of 1-1.5 molar.

First cycle raffinate is concentrated to 1.95 molar aluminum nitrate before being sent to permanent storage. Three mixer-settlers are used in cleaning up the spent solvent (ICR) before reuse. As indicated on the flowsheet, the solvent is washed with dilute nitric acid, 0.05 molar sodium carbonate, and again with dilute acid. The first acid wash is used to make sure that no aluminum nitrate solution (overflow from the A and B columns) accidentally gets into the carbonate wash, where it would precipitate and plug up the mixer-settler. The carbonate wash removes fission products from the solvent and prevents their accumulation. The final acid wash reduces the tendency of the solvent to form emulsions when re-introduced in the IA column.

The flowsheet for the hexone cycles is more straightforward than that for the TBP cycle, in that no recycle streams are involved nor are there any devices for removal of degradation products. The second cycle scrub is 2.0 molar aluminum nitrate made highly basic with ammonium hydroxide (short of precipitation of aluminum) because of the large amount of acid present in the feed stream. The second cycle scrub also contains ferrous sulfamate (ferrous ammonium sulfate and sulfamic acid) to effect plutonium removal. In the extraction section of the compound column, the aluminum salting strength is maintained at 1.5 molar, with a 0.2 molar "acid deficiency" (ammonium hydroxide concentration) for optimum decontamination; the aqueous-to-organic ratio is 1:1. As in the TBP system, the strip is slightly acidified water; the aqueous-to-organic ratio in the strip (IIB) column is 0.28:1. The second cycle product is slightly more dilute than the second cycle feed; it is concentrated, this time to 1.5 molar uranium, before being fed to the third cycle.

Third cycle A column salting strength, acid deficiency and flow ratios in the extraction section are similar to those of the second cycle. Because the acid content of the third cycle feed (IIIAF)

is lower than that of second cycle, less ammonium hydroxide is required in the scrub. Strip column aqueous-to-organic ratio is 0.39:1, somewhat higher than in the second cycle because of the higher uranium concentration in the organic feed to the column.

Spent hexone solvent is cleaned up for re-use by mixing 60 volumes of solvent with one volume of 3 molar caustic and steam distilling off the hexone, followed by decantation.

3. Criticality

Since enriched uranium is processed at the ICPP, criticality control must be exercised throughout the process equipment, not only in those vessels which normally contain uranium but also in those items of equipment which should not contain uranium but because of process upsets or equipment failure may do so.

The charging cave contains no water and precautions are taken to see that none is admitted to it. A very large quantity of fuel may thus be permitted in it without danger, although as a matter of policy, only slightly over a charger load is allowed. The continuous dissolvers are geometry limited; they can be, and are, filled with fuel regularly. Even though the dissolver voids are filled with dissolved fuel solution, it is sub-critical. Feed tanks and the run tank are four-foot diameter vessels but the concentration of uranium in them is limited by the gross amounts of aluminum in the fuel to less than a critical concentration.

The extraction columns are also concentration limited, although here greater care must be exercised since it is possible to separate and concentrate the uranium in them. In general, flow ratios and "cold" stream concentrations are carefully checked to prevent the over-concentration of uranium through internal reflux. The tube bundle and cold leg of the first cycle product evaporator are geometrically safe for uranium solution of any concentration. The vapor disengaging space is of non-safe diameter (two feet) but is prevented from accumulating a critical mass of solution by an over-flow line.

First cycle raffinate cannot contain appreciably more uranium than is present in the feed and is therefore handled in four-foot vessels without special precautions.

The second and third cycle columns, including the column heads, are infinitely safe. Since second and third cycle raffinates and spent solvent could contain a non-safe concentration of uranium, these streams are collected in infinitely safe vessels and transferred to larger vessels only after chemical analysis has shown they contain a safe concentration of uranium. There are no installed

continuous instruments at the ICPP to monitor the uranium content of any streams with the exception of density instruments on the intercycle evaporators.

4. Waste Disposal

Column raffinates are concentrated to about 1.9 molar aluminum before being sent to permanent waste storage. A continuous thermosyphon evaporator is used for first cycle wastes from the TBP system; all hexone cycle wastes are evaporated in batch evaporators.

As indicated in Dr. Stevenson's paper, wastes from the aluminum fuel head-end systems, as well as second and third cycle raffinates, are stored in 300,000 gallon tanks. The tanks are vertical, 50 feet in diameter by 21 feet high at the eaves and are enclosed in concrete vaults with jets discharging from vault sumps to individual tanks. Types 304L and 347 stainless steel have both been used for tank construction; the lower sides and bottom are 5/16 inch thick; the upper sides and top are 1/4 inch thick. Cooling coils in the first of the six cooled tanks consist of 2,100 square feet of 1 inch pipe. Design duty on the coils in the first tank is 1.5 million BTU per hour. Coils are segregated into two parallel systems so that should one leak, the other may be used. Maximum tank temperature has been set at 55°C. Within 4-5 years after filling, wastes in first cycle tanks have decayed sufficiently so that cooling is no longer required. The tanks are equipped with thermowells and density and liquid level probes and are interconnected with steam jets so that the contents of any tank (first or second cycle) may be transferred to any other tank.

Incidental plant wastes are stored with second and third cycle raffinates in tanks similar to the first cycle tanks with the exception that the cooling coils are omitted. Both first and second cycle tanks are vented through 10 inch vent lines to water cooled condensers and thence through a 12 inch manifold to the stack. Condensate from the condensers is drained back to the appropriate tank.

Construction of a demonstrational fluid bed waste calciner is under way at the ICPP; completion is expected in mid 1960. Design capacity is 60 gallons of waste per hour. Nitrates will be decomposed and discharged to the stack; aluminum and fission products will be converted to the oxides and stored as solids. An overall volume reduction factor of about eight is expected.

B. Batch Process

The batch dissolution process for aluminum fuel is the older of the two head ends and has the smallest design capacity (three kilograms of uranium per day from MTR elements). It will likely be

used only for fuel elements which we do not desire to cut up and which are too long for the continuous dissolution system, or with respect to which arrangements have been made for precise burn-up data to be obtained at the ICPP, or for short processing runs consisting of only a small amount of fuel.

1. Flow Diagrams and Equipment

Figure 4 illustrates schematically one of the four batch dissolving lines. The dissolvers, coarse feed, and fine feed adjustment vessels are 3 feet in diameter with a working volume of some 600 liters. Provisions exist for filtration of the dissolver product after the input measurement and initial adjustment have been made in the coarse feed adjustment vessel. The filter systems have not been used in recent years, except for one short-term test.

Limitations on the size of fuel that may be processed in this equipment are set by the curves in the slug chutes and by the diagonal clearance provided for the fuel to drop from the slug chute in the dissolver. The slug chutes are 10 inches in diameter and contain six and seven-foot radius curves to prevent the emergence of a radiation beam from the dissolvers. Tests have demonstrated that a three inch square by 46 inch long element will negotiate the slug chute curves. However, an element longer than 38 inches will not fall free of the slug chute in the dissolver. Normally four MTR elements constitute a batch in these dissolvers; with elements longer than 38-inches it is believed likely that a second element would remain entirely within the slug chute until the first had disintegrated sufficiently to fall into the dissolver.

Following the fine feed adjustment tank the dissolver solution is ready for the hexone extraction columns. The first hexone cycle is schematically identical to the second and third cycles illustrated in Figure 3. Physically, the first cycle columns are of somewhat larger diameter, 5.0 inches rather than 2.0 inches because of the large relative amount of diluent aluminum that is handled in the first cycle, and the A column is longer (37.4 feet).

2. Chemical Flowsheet

Table 2 is the chemical flowsheet for batch dissolution and hexone solvent extraction of MTR fuel. Dissolution of four MTR elements requires 520 liters of 5.33 normal nitric acid containing 0.004 molar mercuric nitrate and about 3 hours dissolution time at boiling. Air is added to the dissolver for nitric acid regeneration, resulting in an acid consumption of 3.6 mols per mol of metal dissolved. The input samples are taken from the coarse feed tank, after which ammonium hydroxide is added to give the proper "acid deficiency" and the solution is transferred to the fine feed adjustment vessel. Following boil-down to the proper concentration the solution is ready for the extraction columns.

Excess salting strength in the first cycle extraction column is provided by the aluminum in the fuel; it is partially

Fig. 4—Batch aluminum-uranium alloy feed preparation.

TABLE 2

Part 1 - BATCH DISSOLUTION FLOWSHEET FOR MTR ELEMENTS

4 MTR Fuel Elements Per Batch - 30 Percent Burnup
 4 1/2 Dissolvings Per Day for 3.0 kgs/day Uranium

		Metal Charged Per Diss.	Dissolver Reagent*	Dissolver Product	NH ₄ OH Adjustment	Column Feed
Volume	1/batch		520	502	44.1	367
Density at 25°C	g/cc		1.151	1.226	0.898	1.307
HNO ₃	<u>M</u>		5.33	1.04		
Hg(NO ₃) ₂	<u>M</u>		0.004	0.004		0.006
Al(NO ₃) ₃	<u>M</u>			1.24		1.70
NH ₄ NO ₃	<u>M</u>					1.42
NH ₄ OH	<u>N</u>				14.0	0.26
Aluminum	g/batch	16840				
Uranium	g/batch	657				
Uranium	g/liter			1.31		1.79
F.P.	g/batch	204				

*Air addition to the dissolver: 2.6 SCFM for 1st hour of dissolution;
 1.3 SCFM remaining 2-4 hours.

TABLE 2

PART 2 - MTR SOLVENT EXTRACTION FLOWSHEET - P CELL FIRST CYCLE

RATE: 3 Kg/day

	<u>FLOW</u> <u>l/hr</u>	<u>Sp.G</u> <u>25°C</u>	<u>HNO₃</u> <u>N</u>	<u>Al(NO₃)₃</u> <u>M</u>	<u>NH₄OH</u> <u>N</u>	<u>NH₄NO₃</u> <u>M</u>	<u>URANIUM</u> <u>g/l</u>
IAF*	70	1.307		1.70 0.006 M Hg (NO ₃) ₂	0.26	1.42	1.79
IAS	8.76	1.153		1.0	0.20		
IAX	58.9	0.80 (Hexone)					
IAR	79.8	1.272		1.60 0.005 M Hg (NO ₃) ₂	0.25	1.25	1.6x10 ⁻⁴
IAP	59.6	0.80					2.10
IBX	15.8	1.002	0.02				
IBR	58.3	0.80					2.2x10 ⁻⁴
IBP	15.8	1.032	0.02				7.94
IIAF	0.35	1.503	0.90				353

* See Table 1 for key to stream designations.

TABLE 2 (Continued)

PART 3-MTR SOLVENT EXTRACTION FLOWSHEET-Q CELL SECOND AND S CELL THIRD
CYCLES

RATE: 3 Kg/day

	<u>FLOW</u> <u>l/hr</u>	<u>Sp. G</u> <u>25°C</u>	<u>HNO₃</u> <u>M</u>	<u>Al(NO₃)₃</u> <u>M</u>	<u>NH₄NO₃</u> <u>M</u>	<u>NH₄OH</u> <u>N</u>	<u>URANIUM</u> <u>g/l</u>
IIAF	0.35	1.503	0.90	2.0			353
IIAS	1.03	1.317				0.60	
		0.05 M Fe (NH ₄) ₂ (SO ₄) ₂ and 0.10 M HSO ₃ NH ₂					
IIAX)							
IIIAF)	1.39	0.80	(Hexone)				
IIAR	1.37	1.254		1.52	0.23	0.21	0.009
		0.04 M Fe(NH ₄) ₂ (SO ₄) ₂ and 0.08 M HSO ₃ NH ₂					
IIAP	1.41	0.93					88.0
IIIBX)							
IIIBX)	0.50	1.002	0.04				
IIIBR)							
IIIBR)	1.39	0.80					0.009
IIIBP	0.51	1.365	0.04				242
IIIAF	0.35	1.477	0.06				353
IIIAS	1.03	1.310		2.0		0.28	
IIIIAR	1.35	1.244		1.54	0.01	0.20	0.009
IIIIAP	1.41	0.93					88.0
IIIBP	0.51	1.398	0.04				242
PROD.	0.35	1.477	0.06				353

compensated for by the scrub which contains less aluminum than the 1.5 molar concentration required in the extraction section of the column for proper uranium recovery. Scrub flow rate seems to have little effect on overall three cycle uranium decontamination; at times it has been reduced to only a few percent of the feed stream. The aqueous-to-organic ratio in the extraction section of the A column is 1.35:1.

Stripping is again accomplished with slightly acidified water, at an aqueous-to-organic ratio of 0.27 to 1. The B column product is concentrated to 1.5 molar uranium for feed to the second cycle.

The second and third cycle flowsheets are similar to those employed with the CPM systems. There is less acid in the second cycle feed from the hexone first cycle than from the TBP first cycle and as a consequence, the second cycle scrub contains less ammonium hydroxide. The "acid deficiency" and salting strength at the feed tee in the second and third cycle A columns are the same, as are the aqueous-to-organic ratios. In the B columns, the aqueous-to-organic ratio is as in the previous third cycle flowsheet (Table 1), again because of the high concentration of uranium in the organic feed to the columns.

3. Criticality

The major items of concern with respect to nuclear safety in the batch system are the dissolvers. It is impractical to dissolve completely all fuel in each batch; for increased overall dissolution rate, a "heel" is left after each dissolution. Obviously if the cumulative heel became too large, a nuclear incident would result. A statistically designed control chart* is kept for each dissolver to determine when the allowable amount of uranium has been reached. At this point, repeated dissolutions are made without the addition of fuel ("heel cleanouts") until the dissolver is empty.

As with the continuous processing system, the high ratio of aluminum to uranium in the dissolver product limits the concentration of uranium that may be achieved in the adjustment vessels and filters. The IA column raffinate likewise could not contain a high concentration of uranium; nevertheless, it is accumulated in infinitely safe tanks and analyzed before being transferred to batch evaporators for buildown. The first cycle columns are of infinitely safe diameter, as are the second and third cycle columns, which have already been discussed.

*Vance, F. P. and Tingey, F. H., "Evaluation of Process Variables in the Recovery of Spent Reactor Fuel," Chem. Engr. Prog., 52, 375-80 (1956).

Salvage operations are particularly hazardous. Storage of salvage materials is in infinitely safe tanks; only a few non-safe vessels are involved. A careful record is kept and frequent analyses made on the contents of these vessels; not more than 800 grams of uranium is allowed in all the non-safe vessels combined, and recycle to the process is accomplished in not more than 800 gram batches, added to the IA column feed batches with vigorous agitation.

4. Waste Disposal

As with the continuous processing system, the column raffinates are evaporated and stored. Second and third cycle waste handling is identical to that described previously and is accomplished in the same equipment. First cycle waste concentration is carried out in a batch rather than a continuous evaporator; the concentration achieved is the same.

II. ZIRCONIUM FUEL REPROCESSING

A. Flow Diagrams and Equipment

The zirconium head-end at the ICPP was designed for reprocessing fuel from the Nautilus. It consists of a single batch dissolver and a set of first cycle extraction-stripping columns. The columns are also used for the processing of stainless steel fuel and employ a TBP extraction system. They are quite small compared to the TBP columns for aluminum fuel and have a correspondingly smaller capacity.

Figure 5 illustrates schematically the dissolver-feed adjustment system. The diameter of the lower portion of the dissolver is 24 inches; that of the upper portion, 42 inches. Minimum wall thickness is 3/8-inch. The slug chute is 14 inches in inside diameter. There are no curves in the slug chute; it is a straight fall from the charging cask to the dissolver. Shielding over the slug chute is provided by a lead slide valve. The impact of the heavy elements is absorbed by a 6-inch thick crash plate in the bottom of the dissolver. The working volume of the dissolver is 750 liters with an ultimate capacity of 1825 liters. The dissolver is made of monel. Corrosion allowance is 3/16-inch. Preliminary corrosion work indicated rates as high as 0.05 inches per month, or a 2700-hour life. A corrosion specimen in the dissolver for 244 hours of exposure gave an indicated rate of 0.007 inches per month, or 18,500 hours life. The small amount of nitric acid used to dissolve the tin in Zircaloy is more corrosive to the dissolver than the hydrofluoric acid used for dissolution of the zirconium.

The coarse feed adjustment vessel is made of Carpenter 20; the other vessels are of type 347 stainless steel. Corrosion rates are held to quite acceptable values by the use of aluminum nitrate

Fig. 5—Zirconium feed preparation.

complexing agent which is put in the coarse feed adjustment vessel before the dissolver solution containing excess hydrofluoric acid is jetted to it from the dissolver.

There are no provisions for filtering or clarifying the dissolver product.

Figure 6 illustrates the first cycle extraction-stripping process for zirconium fuel. There are four columns as in the aluminum process; however, the arrangement is somewhat different. Since the A column waste contains fluoride and requires costly tankage, it is desirable to keep its volume to a minimum. Therefore the B (scrub) column is a compound column, the lower portion of which re-extracts and recovers uranium from the spent scrub. Thus the spent scrub (IBR) may be sent directly to aluminum waste storage, since it contains no fluoride or appreciable quantities of uranium. In the continuous aluminum system, the spent scrub was mixed with fresh feed and sent to the IA column for uranium recovery.

In summary, uranium is extracted from the fluoride-containing dissolver product in the IA column, scrubbed for additional fission product decontamination in the IB column, and stripped from the organic phase in the IC column. The ID column is again a wash column, to remove TBP and degradation products from the strip column product before concentration in the first cycle product evaporator.

Uranium solution from the evaporator is sent to the second and third cycle hexone columns which have been discussed in connection with aluminum fuel reprocessing.

The A column is 2.9 inches in diameter (I.D.) with an actual length of 21 feet. The B column scrub (upper) section is 1.9 inches in diameter by 6.6 feet long; the extraction section is 1.25 inches in diameter by 12.2 feet long. The C column is 1.9 inches by 13 feet. All are pulsed, sieve plate columns. The D column is a packed column, 1.25 inches by 10 feet.

There is no A column waste evaporator; laboratory work indicated that the solution was near saturation and that heating it would hasten the precipitation of solids. The A column wastes are stored as they come from the column. B column wastes are routed to a batch evaporator where they are concentrated and sent to the first cycle aluminum waste storage tanks.

The solvent is cleaned up for re-use in four mixer-settlers. Sodium carbonate solution, dilute nitric acid, caustic solution, and a second dilute nitric acid wash are used in sequence.

B. Chemical Flowsheet

Fig. 6—Schematic of TBP first cycle for zirconium fuels.

Table III is a proposed flowsheet for the processing of PWR seed material. It is based upon the dissolution of two sub-assemblies per batch and three dissolution batches per day, for a total uranium throughput of 2.56 kg per day. The fuel and 100 liters of water are placed in the dissolver initially. The 10 molar hydrofluoric acid is metered in over a period of several hours. After a short induction period the reaction proceeds vigorously and is limited by the acid addition rate. Following the hydrofluoric acid addition, the one molar nitric acid is added to oxidize the tin in the Zircaloy and the dissolver product is transferred to the Coarse Feed adjustment vessel containing the Coarse Feed adjustment solution. Generally a second adjustment is not required and the solution is ready for introduction into the extraction columns.

The feed is a stable solution over only a limited range of fluoride and zirconium concentrations, and aluminum is necessary as a salting agent in the 1A columns. The Coarse Feed adjustment solution is designed to assure that both of these conditions are met, as well as to oxidize the uranium to the VI valence state.

It has been found that the aqueous-to-organic ratio in the A column can be raised to 8:1 with satisfactory uranium recovery. The B column scrub solution is 0.7 molar aluminum nitrate; in addition to removing fission products it also strips most of the acid from the organic phase that was picked up in A column. Stripping in the C column is accomplished with 0.01 molar nitric acid at an aqueous-to-organic ratio of 4:1. TBP and degradation products are washed from the uranium strip solution in the 1D column with virgin hydrocarbon diluent (Amsco 125-90W). There is no steam stripper; after concentration to one molar uranium, the evaporator product is ready for introduction into the second hexone cycle.

The hexone second and third cycle flowsheets are now shown, but are quite similar to those used for aluminum fuel.

C. Criticality

The major item of concern with respect to nuclear safety is the dissolver. Present ICPP practice does not allow more than 1700 grams of total uranium in the dissolver at any one time, based on uranium content before irradiation. As with the batch aluminum dissolvers, a statistically designed control chart is used to ensure that the limit is not exceeded and heel cleanouts are made as required by the control chart.

By way of brief explanation, the maximum total uranium content of the dissolver is limited to 1700 grams on the basis that 1700 grams of uranium-235 is the minimum amount that can go critical when contained as a homogeneous solution in a 23 1/4-inch diameter vessel (the dissolver diameter). Also, this is considered the worst

1.5% J

TABLE 3

PART 1 - PROPOSED PWR DISSOLUTION FLOWSHEET

<u>Stream</u>	<u>Dis.</u> <u>Re-</u> <u>Agt.</u> (1)		<u>Dis.</u> <u>Prod.</u>	<u>Dis.</u> <u>Wash</u>	<u>Coarse</u> <u>Feed</u> <u>Adj.</u> <u>Soln.</u>	<u>Coarse</u> <u>Feed</u>	<u>IAF</u>
L/Batch	276	13.6	372	44	592	1040 ⁽²⁾	1120 ⁽³⁾
SpG							
25° C	1.067	1.033	1.25	1.0	1.20	1.21	1.20
U g/l			2.30			0.820	0.763 -
Zr M			1.65			0.59	0.55
Al M					1.42	0.81	0.75
Sn M			0.019			0.0070	0.0065
Cr M					0.026	0.015	0.014
H M	10.0	1.0	0.786		1.0	0.85	0.79
F M	10.0		7.43		1.0	3.22	3.0
NO ₃ M		1.0	0.024		4.26	2.44	2.27
H ₂ O L				44			

(1) Dissolver charge consists of two subassemblies after 40% burnup, estimated to contain 56 kg of zirconium 854 g of uranium and 860 g of tin, and 100 liters of water.

(2) Includes 32 liters jet dilution.

(3) Contains 80 liters jet dilution.

1.5700

TABLE 3

PART 2 - PROPOSED PWR FIRST CYCLE EXTRACTION FLOWSHEET
Three Dissolver Batches Per Day

	<u>Flow</u> <u>l/hr</u>	<u>SpG</u> <u>25°C</u>	<u>Uran.</u> <u>g/l</u>	<u>NO₃</u> <u>M</u>	<u>H</u> <u>M</u>	<u>Al</u> <u>M</u>	<u>Zr</u> <u>M</u>	<u>F</u> <u>M</u>
IAF	140	1.20	0.763	2.27	0.79	0.75	0.55	3.0
			0.0065 M Sn and 0.014 M Cr					
IAX	17.5	0.78			(10% TBP)			
IAR	140	1.19	0.00076	2.23	0.75	0.75	0.55	3.0
			0.0065 M Sn and 0.014 M Cr					
IAP	17.5	0.79	6.10	0.32	0.16			
IBS	8.75	1.11		2.10		0.70		
IBX	3.42	0.78			(10% TBP)			
IBR	8.75	1.12	0.0012	2.71	0.31	0.70		
IBP	20.9	0.79	5.10	0.03	0.01			
ICX	5.25	1.00		0.01	0.01			
ICR	20.9	0.78	0.00051		(10% TBP)			
ICP	5.25	1.06	20.3	0.13	0.05			
IDS	0.525	0.76			(AMSCO)			
IDR	0.525	0.76						
IDP	5.25	1.06	20.3	0.13	0.05			
Evap. Prod.	0.454	1.32	235	1.50	0.58			

MIXER-SETTLER SCRUB STREAMS

	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
Flow, l/hr	3.3	3.3	3.3	3.3
SpG @ 25°C	1.050	1.002	1.004	1.002
HNO ₃		0.01		0.01
Na ₂ CO ₃ M	0.5		NaOH 0.01 M	

possible condition as a non-homogeneous mixture of fuel and dissolving solution would require more than 1700 grams of uranium-235 to form a critical mass.

Nuclear safety problems in the columns, mixer-settlers and waste tanks are similar to those discussed in the aluminum processing columns and are solved in similar fashion.

D. Waste Disposal

The A column raffinate is sent to permanent storage without any evaporation or other treatment. There are three tanks at the ICPP for the storage of zirconium-type wastes. Each is 11 feet in diameter by 38 feet long, fabricated from type 316 L stainless steel. The shells are 11/16- inch thick; head thickness is 9/16- inch. The tanks set on a concrete pad but are not enclosed in a vault. The tanks were protected with two-inch lumber and the fill was replaced and compacted around them. Design life of the tanks was 10 years but corrosion specimens exposed to wastes in one of the tanks indicate that their life should be 35 - 40 years.

All three tanks are equipped with cooling coils designed to remove 70,000 Btu per hour from each tank. There are four coils in each tank, each coil consisting of 140 feet of 1-inch schedule 160 pipe. Two coils in each tank were considered as spares for the other two.

Filled completely, each tank would hold 30,710 gallons. Each tank is filled to only 90 per cent of its capacity, however, to allow the entire contents to be jetted to a spare tank in case of failure.

As was indicated, the B column waste from the zirconium process is similar to waste from the aluminum processing system and is stored in the first cycle aluminum waste tanks.

III. STAINLESS STEEL FUEL PROCESSING

At the time of writing, the processing of Organic Moderated Reactor Experiment fuel is underway at the ICPP in equipment designed for fuel from the submarine Seawolf. Although the batch dissolver is too small for complete dissolution of an OMRE element in one cut, the fuel is being handled successfully. Dissolver capacity, together with the need to remove an organic coating from the elements in the dissolver before dissolution is started and nuclear safety requirements, limit the processing capacity to about one element per day.

A. Flow Diagram and Equipment

The zirconium and stainless steel processing equipment occupy two cells and were built at the same time. Different dissolvers are

required for the two kinds of fuel, but all other equipment is used in common for both fuels. It is therefore impossible to process both fuels at the same time.

The stainless steel dissolver is essentially a 5.5-inch I.D. pipe 24 feet long, suspended from the ceiling of the cell. Fuel is dropped directly into it from the charger; the limiting diameter is a 5-inch throat in the slide valve assembly which is used to close off and shield the dissolver. As are all dissolvers at the ICPP, the stainless steel dissolver is provided with a condenser as the dissolution is carried out at boiling. The dissolver is jacketed and may be either heated or cooled. Material of construction is Carpenter 20. Working volume is 70 liters. Walls are one-half inch thick, including a corrosion allowance of 0.125 inch. Predicted life, based on the corrosion allowance, is 1.67 years at boiling with 6 molar sulfuric acid and 4.4 years at boiling with 4 molar sulfuric acid.

B. Chemical Flowsheet

Table IV is the chemical flowsheet used for processing OMRE elements. As received, the elements are coated with a carbonaceous deposit resulting from the organic moderator. Laboratory work showed that a 240-gram per liter solution of Turco 4502 (Turco Products, Inc., Los Angeles) at boiling would dissolve it in two hours. (Turco 4502 is a proprietary compound, apparently a mixture of caustic and potassium permanganate.) The Turco solution is discharged to waste after use and the dissolver washed with water.

Forty liters of 6.5 molar sulfuric acid are added to the dissolver following the water wash and the introduction of a pad of steel wool to trigger the dissolution reaction. At the end of three hours at boiling, the dissolver is cooled and 20 liters of 6 molar nitric acid are added to dissolve the uranium dioxide that has been exposed by the dissolution of stainless steel. The solution is again heated to boiling and after a few minutes, cooled and transferred to the Coarse Feed Adjustment Tank to which has previously been added concentrated nitric acid.

The nitric acid added to the dissolver passivates the undissolved stainless steel; as a consequence, the dissolver is washed free of nitrate ion before the second cut is made. Steel wool is again used on the second cut to depassivate the fuel.

The dissolver product from the second cut is added to the first, the input samples are taken, and the solution is transferred to the Fine Feed Adjustment Tank as column feed (IAF).

Although extraction is carried out in the same equipment as that used for zirconium feed reprocessing, there are significant differences in the flowsheet. There is no aluminum present in the A

TABLE 4

PART 1 - BATCH FEED PREPARATION FOR OMRE FUEL ELEMENTS

One OMRE Fuel Element per Batch, Two H_2SO_4 and Two HNO_3 Dissolutions per Element

- A. Turco Bath; 25 liters/batch, - 240 grams/l Turco (4502)
 B. Water wash after Turco; 25 liters/batch pure water.
 C. Dissolver Reagents - Both dissolutions (cuts) are the same.
 One OMRE element contains an estimated 8300 g of 304L stainless steel, 800 g of uranium in the form of UO_2 , and 83 g of fission products. Steel wool must be charged before each cut to initiate the reaction.
 The dissolver must be purged with nitrogen before each H_2SO_4 dissolution.
 1. H_2SO_4 - 6.5 M; 40 liters/batch; Sp.G. 1.24 at 25°C.
 2. HNO_3 - 6.0 M; 20 liters/batch, Sp.G 1.19 at 25°C.
 D. Dissolver washes for two dissolutions - 180 liters pure water/batch. Includes four 45 l H_2O washes, three the first cut and one the second cut. Additional washes as required may be sent to waste to lower nitrate ion for second H_2SO_4 dissolution. Nitrate ion to be reduced to 0.01M in last wash in both cases.
 E. Course Feed Adjustment Solution - 13.0M HNO_3 ; 1.367 Sp.G. at 25°C; 83 liters/batch.

	<u>Dissolver Product^(a)</u>	<u>Coarse Feed^(b)</u>	<u>IAF^(c)</u>
	<u>Each Cut</u>		
Liters/batch	60	406	436
Sp.G 25°C	1.29	1.16	1.150
SS, g/l	69.1	20.4	90.0
Fe, g/l	49.2	14.5	13.5
Fission Prod. g/l	0.69	0.20	0.19
Uranium, g/l	6.67	1.97	1.83
H, M	7.28	4.81	4.48
SO_4 , M	4.33	1.28	1.19
NO_3 , M	1.83	3.23	3.01

(a) Based upon a presumed 50% dissolution for both iron and uranium on each cut.

(b) Includes 23 liters of jet dilution.

(c) Includes 30 liters of jet dilution.

TABLE 4

PART 2 - OMRE TBP FIRST CYCLE EXTRACTION FLOWSHEET
Based on One Dissolver Batch Per Day

	<u>Flow</u> <u>l/hr</u>	<u>SpG</u> <u>25°C</u>	<u>Uran.</u> <u>g/l</u>	<u>H</u> <u>M</u>	<u>NO₃</u> <u>M</u>	<u>SS</u> <u>g/l</u>	<u>SO₄</u> <u>M</u>	<u>TBP</u>
IAF	18.2	1.150	1.83 (0.19 g/l fission products)	4.48	3.01	19.0	1.19	
IAX	10.4	0.781						10%
IAR	18.2	1.145	0.0018 (0.19 g/l fission products)	4.34	2.87	19.0	1.19	
IAP	10.4	0.791	3.19	0.24	0.24			10%
IBS	5.21	1.109	(plus 0.70 M Al(NO ₃) ₃ & 0.04 M NH ₄ OH)					
IBX	2.08	0.781						10%
IBR	5.21	1.128	0.0064 (plus 0.70 M Al(NO ₃) ₃ & 0.04 M NH ₄ NO ₃)	0.44	0.44			
IBP	12.5	0.785	2.66	0.003	0.003			10%
ICX	3.12	1.002		0.01	0.01			
ICR	12.5	0.781	0.0027					10%
ICP	3.12	1.014	10.66	0.022	0.022			
IDS	0.31	0.757						Amsco
IDP	3.12	1.014	10.66	0.022	0.022			
IDR	0.31	0.757						
Evap. Prod.	0.142	1.334	235	0.49	0.49			

MIXER-SETTLER SCRUB STREAMS

	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
Flow, l/hr	3.3	3.3	3.3	3.3
SpG, @ 25°C	1.050	1.002	1.004	1.002
HNO ₃ , M		0.01		0.01
NaOH, M			0.01	
Na ₂ CO ₃ , M	0.50			

column; all salting strength is furnished by nitric acid. The aqueous-to-organic ratio is 1.75:1, although this is not critical and can vary appreciably. In the zirconium process, the ratio was 8:1. The 1B column scrub solution is aluminum nitrate containing 0.04 molar ammonium hydroxide to give improved acid removal in the 1B column. First cycle product is one molar uranium solution, as in the zirconium process.

Preliminary indications are that decontamination performance and uranium losses in the TBP first cycle for stainless steel fuels are comparable to those in the TBP first cycle for aluminum fuels.

Second and third cycle flowsheets are not given but are similar to those presented for the aluminum process.

C. Criticality

The stainless steel dissolver is geometrically safe for any fuel containing a large proportion of diluent metal as well as for any quantity of uranium slurry or for any homogeneous solution. The Coarse Feed Adjustment Vessel is of non-safe diameter, however, and controls must therefore be exercised with respect to the quantity and form of uranium transferred to it. Present regulations allow not more than 1600 grams of uranium-235 in the adjustment vessel as a solution, or not more than 800 grams as a slurry.

Extreme care is taken to ensure that the 6 molar nitric acid solution is added to the dissolver at the end of each cut and that the dissolver is heated to dissolve the uranium dioxide slurry that results from the sulfuric acid dissolution. A control chart is also kept on the dissolver contents to ensure that the dissolver content never exceeds 1600 grams and that therefore no more than 1600 grams will be transferred to the adjustment vessel.

Nuclear safety throughout the rest of the system has been discussed under zirconium fuel processing.

D. Waste Disposal

Stainless steel wastes are not evaporated but rather are stored as they come from the 1A column, as is true with zirconium wastes. There is one storage tank for stainless steel wastes at the ICPP; with the exception of the cooling coils, it is identical to the tanks for zirconium waste storage. There are 12 coils in the tank for stainless steel waste, each consisting of 70 feet of one-inch schedule 160 pipe. Six of the coils are designated as spares. The six in service were designed to remove 200,000 BTU per hour. Corrosion allowance on the tanks for both zirconium and stainless steel wastes is one-fourth inch. No data have been obtained as yet on corrosion rates with actual stainless steel wastes.

B column wastes are concentrated and sent to first cycle aluminum waste storage as in the zirconium process.

IV. CONCLUSIONS

Facilities exist at the ICPP for processing highly enriched fuel containing aluminum, zirconium, or stainless steel alloying materials. The equipment for zirconium and stainless steel fuels is of small size with a resultant low throughput, although the dissolvers can handle full-sized charges of fuel. A trained staff, analytical facilities, maintenance facilities, product handling facilities and fuel storage facilities are on hand. Fuel can be received either by rail or truck, and a large, heavily shielded hot cell is available adjacent to the basin for installation of mechanical disassembly equipment. The various processes are proven, having been operated for periods varying from a few months to several years.

ICPP INPUT MEASUREMENT PROGRAM

by

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The measurement of SS Material introduced to process and on which accountability is based, is that identified with the dissolver solution run tank. For the continuous dissolver process the dissolver solution of $\text{Al}(\text{NO}_3)_3$, HNO_3 , $\text{UO}_2(\text{NO}_3)_2$ and fission products is filtered by gravity as it flows continuously to the run tanks through line coolers. Two dissolver run tanks provide surge capacity and a means for measuring the volume and composition of a run tank batch. For the batch system, the dissolver solutions are transferred (after a predetermined dissolution time) by steam jet eduction to the run tanks. For a minimum of thirty minutes prior to sampling the run tank solution is air-sparged in order to provide thorough mixing. The sparge time (thirty minutes) was established from a designed experiment in which heterogeneous solutions simulating dissolver effluent were sparged for various time periods, sampled and analyzed in replicate, and tested for significant variations.

Special sampling equipment is required for the dissolver solution because of the high level of radioactivity present. A sampler system (1) somewhat different from that used at other AEC sites was designed to meet the particular needs of this plant. Special sampling corridors were constructed at operating corridor level for each cell tank. Samplers for several cells were grouped so that a continuous 4.5-inch lead shield having one entry for a sample carrier and a single set of sample handling tongs could be used. The tip of the sampler is fitted with two hypodermic needles that punch through the neoprene cap on the sample bottle. Sample bottles are removed from the sample carrier, conveyed to the sample jet and raised to sampling position. The sample is drawn by drawing a vacuum on the bottles through a sharp needle with the jet, which in turn, draws process solution from the vessels through the sampling line and the long needle into the bottle. The solution is circulated through the bottle and returned

to the process vessel for a few minutes before the jet is turned off and the bottle removed. The sampling operation is viewed through a lead-glass window located directly in front of the sampler. The filled sample bottle is returned to the sample carrier and removed from the sampling station for delivery to the analytical facilities. The sampler stations are equipped with steamers that are used to steam the intake and discharge lines in case of plugging. The steamers are also used during sampler decontamination operations.

Three 5-ml samples are drawn from each dissolver batch run tank solution. The first sample from a given batch is circulated a minimum of fifteen minutes through the sample bottle so as to purge the sample draw lines. The subsequent two samples are circulated a minimum of five minutes each.

Routinely, acidity and specific gravity are determined on each of two of the three samples drawn from each batch. Rerun or range limits, determined by applying the method of mathematical statistics to experience data relative to the analytical error and sampling error to be associated with a particular measurement, are provided as a safeguard against nonrepresentative samples and/or analyses. Depending upon the agreement of the duplicate specific gravity and acidity determinations, one or two of the samples are prepared for a concentration determination.

Specific gravity and acidity determinations are operational measurements used for process control and are not used for uranium accountability except in an indirect manner such as just described.

Dissolver samples are extremely complex from an analytical chemistry viewpoint, especially for the determination of uranium. Uranium concentrations are relatively low, varying from 1 to 20 grams per liter, compared to the alloying constituent and complexing agents that may have been added. Even more important is the presence of fission products which are present in concentrations comparable to the uranium in these high burnup fuels. The main fission products are elements 36(krypton) to 46(palladium) and 52(tellurium) to 62(samarium) which includes yttrium, zirconium, niobium, ruthenium, iodine, and rare earths. These elements, many of which have multi-oxidation states, undergo reactions similar to uranium in conventional analytical methods for its determination.

A preliminary separation of the uranium from the fission products alloying constituents, and complexing agents adaptable to remote use is required. A liquid-liquid extraction scheme (2) is used for this separation. In this separation, uranium is extracted into an organic solvent, namely, methyl isobutyl ketone. With highly radioactive samples, it is an advantage to have the extracted uranium phase sufficiently low in activity to permit its removal from the expensive and time-consuming remote area for completion of the analysis. The

completion of the analysis is accomplished by the isotopic dilution mass spectrometric method (3). Three distinct advantages and reasons for which this method is used are: quantitative separation of uranium is not necessary (permitting the selection of extraction conditions to give an extremely high decontamination), the mass distribution of isotopes is simultaneously determined on the same sample, and aliquots of samples containing only a few hundred micrograms of uranium suffice.

The bench separations procedure is as follows: To a test tube are added 0.500 ml of a 1.00 mg per ml uranium - 233 standard solution and 4.0 ml of 1N acid-deficient, 2M aluminum nitrate salting solution. If the sample contains uranium in oxidation states lower than $\frac{1}{6}$, 0.1 ml of a 0.1M potassium dichromate solution is added. The test tube is transferred to the remote facility where 0.500 ml of the sample is added from a specially fabricated pipetter (4). The tube is next transferred to the remote extraction box. The solution is shaken for 1 minute to insure homogeneity. Two milliliters of methyl isobutyl ketone are added and the phases are mixed by shaking for 1 minute. As much of the organic phase as possible (without any of the aqueous phase) is transferred from the remote area to a conventional laboratory. The solution is centrifuged, the organic (top) layer is transferred to another test tube, 1 ml of 30% hydrogen peroxide is added which strips the uranium and simultaneously precipitates it as the peroxide. After centrifugation, the precipitate is washed with acetone (to remove last traces of methyl isobutyl ketone) and transferred to the mass laboratory.

In the mass laboratory, the peroxide precipitate is dissolved in a minimum amount of nitric acid and evaporated on tantalum filaments for scanning. The actual concentration is determined from a relationship involving the ratio of the percent spike isotope in the spike material to the same isotope in the spike and sample. The choice of U-233 as the spike isotope is somewhat obvious since the dissolver solutions contain the uranium isotopes U-234, U-235, U-236 and U-238.

Two mass spectrometers (5) are available at ICPP, one constructed by Argonne National Laboratory for use at the Idaho Chemical Processing Plant, the other an improved model constructed by Phillips Petroleum Company personnel. The sample to be analyzed is evaporated from a nitric acid solution onto a filament of tantalum ribbon. The material is deposited as U_3O_8 . A 50-microgram deposit is usually sufficient for analysis. After introduction into the instrument through a vacuum lock arrangement, the filament is heated and ions are emitted by a surface ionization process. The spectrum is scanned to receive UO_2^+ ions. These ions are then accelerated through a potential of approximately 6,000 volts and beam deflection is achieved by a permanent magnet. The masses are scanned electromagnetically by varying the current through a range of 250 milliamperes upon windings around the poles of the permanent magnet. This is done electronically by using an RC time-constant circuit. The ion beam representative of the individual isotope is received and the signal is amplified by an electrometer-type ion detector. The intensities of the ion beams are recorded by a Brown electric recorder as a series of peaks of various

heights on a single roll of paper at preselected amplification factors. Measurement of the peak heights of the total signal affords a relationship from which the weight per cent can be easily calculated.

The isotopic dilution method, although explicit, requires a long analysis time and expensive equipment. Thus, fundamental research and development studies have been made to provide a method less involved and of sufficient precision and accuracy to be used for SS accountability purposes. As a result of such studies the coulometric determination of uranium(VI) (6) at controlled potential has been developed and can, if desired, replace the isotopic dilution method. This method is based on methyl isobutyl ketone separation of tetrapropylammonium uranyl trinitrate from acid-deficient aluminum nitrate solution followed by direct coulometric reduction of uranium(VI) at a mercury cathode. Perchloric acid volatilizes ruthenium and technetium which are the only known interfering species extracted with uranium. The uranium is determined by controlled potential reduction of the citrate complex after a prereduction step to eliminate easily reducible material. The complete procedure requires approximately two and one-half hours. Results on samples from solutions of freshly dissolved aluminum-uranium fuel elements having about 20% burnup show excellent precision and no bias as compared with the previously described isotopic dilution thermal mass spectrometric method.

Rigorous statistical quality control is maintained over all aspects of the data-generating mechanism (7). Run tanks prior to start-up were calibrated under highly controlled conditions. Recalibration is possible only at the infrequent times the cells are decontaminated for maintenance purposes. The calibration procedure requires introducing into the vessel known increments of water as determined by weigh tank measurements corrected for water temperature and scale bias. The resulting volumes are related to direct reading, manometer liquid-level measurements. Statistical analysis of data so generated gives "best" estimates for the parameters of the calibration curve and the associated uncertainty. The choice of calibration curve in any given case depends upon the geometrical properties of the vessel. Usually the vessel approximates a right circular cylinder to a sufficient degree that a linear equation is representative. In some cases, however, as a result of welding laterally around the vessel, distortion is sufficient to require a quadratic type calibration curve or possibly two linear curves defined over different ranges.

Since the accuracy of the calibration is affected by variations in manometer fluid density, the supplier's nominal density is ignored and replicate sample analyses for specific gravity are performed on each fluid used.

As previously mentioned the surveillance for sample legitimacy is exercised by the Shift Control Laboratory through the routine determination of both specific gravity and acidity on each of two of the

three samples routinely taken from each feed batch. Maximum allowable limits for the difference between the two specific gravity analyses is ± 0.003 and for the difference between the two acid analyses $\pm 0.04N$. The limits reflect both sampling error of the homogeneous uranyl nitrate solution and analytical error associated with each method. If both the specific gravity difference and the acidity difference fall within the corresponding limits only a single sample randomly determined from the two samples used, is prepared for isotopic dilution and mass distribution analysis by the Mass Laboratory. In the event the specific gravity and/or acidity ranges fall outside the above limits the Analytical Laboratory analyzes the remaining sample for both acid and specific gravity. The agreement of any two of the three sample analyses available for each component within the appropriate range limits is sufficient basis for selection of one sample for mass and concentration analysis from the two samples which provided the within-range agreement, both acidity and specific gravity-wise. If agreement for both specific gravity and acidity is not obtained one aliquot from each of the three sample bottles associated with a given batch is prepared for mass and concentration analyses.

The Mass Laboratory, under this procedure, analyzes for mass distribution and concentration all samples provided them by the Shift Control Laboratory. For each sample filament three scans are routinely obtained. Protection against malfunction of the instrument with regard to a particular scan is accomplished by comparing, for each isotope, the indicated abundance for each of the three scans. When concentrations are to be determined under the isotopic dilution technique, comparisons between the three indicated concentrations are also made. Thus, on the basis of reproducibility of scans, both maximum ranges and maximum gaps between ordered percentages for each isotope and concentration for each scan can be derived at various confidence levels (8). Significant range along with a nonsignificant gap is sufficient reason to repeat the series of three scans.

Continual surveillance of analytical methods is achieved by randomly submitting control samples, made to simulate plant samples, at a rate of about 3 per 100 plant samples. These samples are of known composition and hence, the continuous monitoring of the bias for each method is accomplished. Approximately 28 routine analytical methods are subjected to this continual type of control. To date, associated with each of these methods we have accumulated over 300 control analyses. These analyses were obtained from a variety of chemists and over an extended period of time, thus providing valuable information for estimation of error components. It is to be noted that this program is primarily directed toward bias control. Precision estimates to be associated with the methods are derived from design programs which include all stages of data generation in measuring plant feed.

In addition to the standards program, a standard solution is analyzed at the beginning of each shift according to the method or

methods to be used that day. Results from this standard must also fall within allowable limits as determined from statistical procedures, before analysis of plant samples begins. This affords protection against malfunctioning equipment and faulty reagents.

Since, in the last analysis, the "quality" of data being generated by any laboratory is most significantly influenced by the competence and training of the analyst, a program directed toward certification of each analyst on each method was initiated at ICPP in December of 1955 (9). This program, very briefly, is as follows: Each technician in the laboratory is given a period of intensive training and practice on part or all of the 28 methods now under this program. When the individual feels that he is qualified on a particular method, nine synthetic control samples are submitted to him for single determinations on each sample. At least three levels of the component under analysis are required. Of course the true levels of the components are withheld from the individual. On the basis of the performance of the entire group of analysts who have successfully passed a given method certain parameters related to bias and precision are computed. These parameters are revised periodically to reflect the effect of increased experience in the program. The corresponding parameters are determined for each analyst's set of nine determinations and are compared by statistical tests with the group values. Under the assumption that group values are, in essence, known, statistical tests are constructed to determine the significance of departures of the individual's parameters from the group. In the event the bias and/or precision associated with a given individual on a given method is significant the individual is given further specialized training after which a repetition of the series is required. For plant processing samples, analysts are restricted to those methods successfully passed.

In addition to the control procedures previously enumerated, error component studies directed toward identification and estimation of source and magnitudes of variation for each analytical method are routinely performed (10). For example, considerable effort in this regard has been directed toward the isotopic dilution method of analysis. In particular, seven sources of variation in addition to sampling have been identified with this measurement. These are (1) day-to-day effect, (2) decontamination and sample preparation, (3) chemist-tester variation and sample preparation, (4) variation between remote pipetters used in sample preparation, (5) differences between the two mass spectrometers used in analyzing the samples, (6) effect of mass spectrometer technician and (7) reproducibility of scans or measurement error.

An experimental program conducted according to statistical design facilitated an estimate of each of these components and in fact, helped define the analytical program for this measurement.

Certain auxiliary controls are available based upon the fission stoichiometry of U-235 (11). The stoichiometric relationship between U-235 fission and U-236 produced by n, γ reaction alloys derivation of equations relating burnup and fission product generation. In particular for a highly thermalized reactor knowing the unirradiated uranium content of the fuel, pre-and post-mass distribution ratios and the capture-to-fission cross section ratio for U-235 one can calculate the stoichiometric residual uranium and/or U-235 content. In the same manner one can construct an expression which relates the residual U-235 to the residual U-236 and consequently serves as an excellent control mechanism over the actual analytical measurements of these components. Clearly the application of the stoichiometric relationship to the residual uranium determination must be to incremental units of fuel charged to the dissolvers as determined by clean dissolver to clean dissolver. Since the calculation depends upon a knowledge of σ (the capture-to-fission nuclear cross section for U-235), preirradiated uranium content, U-236 and U-235 fractions it is necessary that these factors be known to fairly high precision if this computation is to be of value. Usually the unirradiated uranium and mass measurements are available from the fuel fabricator; at any rate if he is alerted to the subsequent need for such measurements they, in all likelihood, will be available. Considerable fundamental research has been accomplished with regard to the value of the capture-to-fission cross section ratio for U-235. From extensive processing data we have estimated it to be 0.185 ± 0.008 (12). Such relationships are extremely valuable for verifying fuel burnup and hence, residual uranium content and residual U-235 content in the fuel to be processed. Through periodic dissolver cleanouts material balances are constructed and a comparison is made among shippers' stated residual content, measured plant inbalance and inputs as calculated stoichiometrically.

Another auxiliary control which is available has to do with constructing an aluminum balance over the dissolver step. For aluminum-uranium alloyed fuels an indicator of possible feed tank bias is routinely effected by the construction of an aluminum balance over the dissolver operation. On the basis of known aluminum charge to the dissolvers as determined from fuel fabrication history, piece count, and the aluminum content of dissolver solutions, as measured in the feed metering tanks, an aluminum balance can be constructed. The aluminum concentration in the feed solution can be measured directly by chemical analysis of the feed sample or indirectly from an empirical relationship (13) which relates specific gravity in the solution to concentration of component parts. At ICPP the latter approach is used since the aluminum analysis of hot feed solutions at best is difficult and considerable experience has been gained in the sensitivity of the empirical relationship to operating conditions. The actual relationship relates specific gravity to aluminum nitrate molarity, nitric acid normality, ammonium nitrate molarity, the uranium concentration, the mercury concentration and the ammonia normality. When the relationship is solved explicitly for aluminum nitrate molarity only the nitric acid

normality, the uranium concentration and the mercury concentration are of any consequence, in addition to the specific gravity. Batch-to-batch average values for uranium concentration and the mercury concentration can be used with negligible consequence; hence, the resulting equation is one by which the aluminum molarity can be predicted as a function of the specific gravity and the nitric acid normality of the solution. As with the stoichiometric relationships an effective balance can only be constructed in incremental units defined by clean dissolver to clean dissolver.

Any discrepancy over and above the uncertainty associated with the calculation is sufficient reason to suspect the input measurements and, in particular, run tank volume measurements if solution concentration measurements are in a state of statistical control as determined by the control mechanism for this measurement as previously discussed.

An alternate use for the aluminum balance equation is that for predicting uranium concentration in a given batch. If one can assume that the percentage uranium dissolved in any batch is the same as the percentage aluminum then the empirical relationship relating specific gravity of the solution to the various component parts can be solved for uranium concentration and, as such, can be used to predict or to estimate the concentration of uranium per batch as a function of the specific gravity, the nitric acid normality, the catalyst concentration and the uranium-aluminum ratio for the charged fuel. Since the aluminum cladding on the fuel elements dissolves more rapidly than does the alloy and extended dissolutions over residual heel tend to concentrate the uranium in the heel some question arises as to the appropriate ratio to use for the uranium-aluminum ratio. As an approximate procedure it has been found expedient to use the uranium-aluminum ratio corresponding to the entire fuel and exclude from the calculation the several batches at the beginning and the end of each dissolver cycle.

For any given measurement system and any given application, the number generated for SS materials accounting purposes has associated with it an uncertainty which is usually expressed as an interval about the measured quantity and has identified with it a probability statement, i.e., the probability is P that the interval constructed contains the true value for the SS material in the batch, core, run, etc. The actual computation of this uncertainty depends upon

- (1) the manner in which the fundamental process measurements combine to give the measurement,
- (2) the random and systematic errors in each fundamental measurement.

The mechanics by which one propagates the component errors to a resulting error in the calculated SS quantity is obtained by means of the differential calculus. A formula called the propagation of errors

(14) formula has been derived which facilitates this computation. As applied to U-235 content of a given segment of fuel measured into ICPP (15), the basic measurements are batch volume, concentration and U-235 fraction. Each basic measurement has both a random and a systematic component. The random component reflects the precision of the corresponding measurement and the systematic component, the bias. Expressed in relative percentage standard deviation units, these have been estimated for ICPP measurements to be:

<u>Component</u>	<u>Random</u>	<u>Systematic</u>
Concentration	2%	.1%
Volume	.3%	.1%
U-235 fraction	.14%	.1%

The propagated percentage standard deviation can be shown to be:

$$\left\{ \frac{1}{n} \left(\frac{2^2}{m} + .3^2 + \frac{.14^2}{m} \right) + \left(.1^2 + .1^2 + .1^2 \right) \right\}^{\frac{1}{2}}$$

$$= \left\{ \frac{1}{n} \left(\frac{4.0}{m} + .09 \right) + .03 \right\}^{\frac{1}{2}}$$

where n is the number of batches and m the number of sample-analyses per batch. For one sample analysis per batch and approximately one-half-kilogram batches approximate 95% limits of uncertainty in total cumulated U-235 input measurements are estimated to be:

<u>Cumulated Input</u> (kg U-235)	<u>Approximate 95% Limit/Uncertainty</u> (kg)
5	.07
10	.10
15	.12
20	.15
25	.17
50	.27
100	.45
150	.63
200	.80
250	.98
500	1.85

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IDAHO - QUESTION AND ANSWER SESSION

"Please discuss, as much as is presently known,
the cost penalty for excess aluminum or stain-
less steel material attached to fuel assemblies."

Response - F. P. Baranowski:

I am not clear on whether this refers to the processing charges, as under the conceptual plant, or the cost penalty to the AEC when actually processing fuels.

As mentioned earlier in the meeting, the processing charge, as computed on the conceptual plant basis, was not scheduled for discussion at this meeting. However, since there are two interpretations to the question, we will answer both interpretations. I will answer the conceptual plant version of the question and Dr. Stevenson will talk about the cost penalty to the AEC during actual processing when aluminum comprises a substantial portion of total metal present as in MTR-type alloy fuels.

In a conceptual plant, there is an effect on the total processing charge to the reactor operator. The more stainless steel or aluminum there is present in the fuel, the lower the uranium processing rate and the longer processing time for a given batch of irradiated fuel. The total processing charge, therefore, increases when the uranium concentration is reduced in the alloy fuels. One can compute the charge penalty for increasing the aluminum-uranium rate in alloy fuels of MTR-type by using a processing rate of 400 kilograms of total metal (uranium and aluminum combined) in the conceptual plant.

I now turn the meeting over to Dr. Stevenson.

By Dr. Stevenson:

I think, as is usual, in comparing a theoretical, let's say, with an actual situation, that the latter becomes more complicated. However, in general, for a given amount of metal processed, total metal, the uranium content doesn't make much difference, as long as

one is dealing with highly enriched materials; that is, if the fuel is primarily aluminum or other diluent metal.

We think of the Idaho plant as an aluminum processing plant, as a zirconium plant, or as a stainless steel plant, and not as a uranium plant. These metals determine the quantities processed below second and third cycle limitations. However, conversely, there is almost an inverse relationship, if you consider quantity processed on the basis of a standard amount of uranium.

A further complication enters when you consider a fuel element which may have a nominal amount of uranium, let's say a couple of hundred grams, but increase the amount of diluent metal. In the case of an OMRE-type element, for example, you could increase this diluent metal to a certain limit which would correspond to the amount of reagent you could put into an existing batch dissolver. Beyond that, you would run into new difficulties caused by requiring double batches, or get to a point where you couldn't conceivably process the material, because a single unit just contains too much stainless steel to handle.

The same would be true with almost any other diluent metal, I think.

"Will single-batch storage times of greater than sixty days be considered? Many prospective users of ICPP facilities consider one hundred and twenty days to be a more reasonable figure."

Response - F. P. Baranowski:

This point will be the subject of discussion tomorrow evening in Building 703-A.

I would like to point out that the meeting room is restricted to around sixty people, and I was requested to ask that those of you intending to be present at the meeting indicate your participation on a piece of paper at the front desk. If more than sixty people attend, we will have to find another conference room.

"Are your casks of such a design that in the event of loss of cask coolant, the heat from the radioactive decay of the elements can be removed by the natural circulation of air within the casks?"

Response - F. P. Baranowski:

I'd like to point out that all of the shipping containers used by the AEC are not under the control of the Division of Production.

In the one type of shipment I am familiar with, calculations have indicated that the decay heat used can be removed at a satisfactory rate.

As we mentioned earlier, the meeting is restricted to the acceptance of the cask at the site, which meets our cask acceptance criteria. We have assumed that the shipping container will meet the regulatory requirements.

I believe the question refers to a proposed regulatory requirement by the AEC. The information on various shipments made by the AEC is being accumulated by the Division of Licensing and Regulations.

I suggest that the person that asked the question check further with the Division of Licensing and Regulations in Washington, D. C.

"Can uranium-aluminum and uranium-stainless steel
fuel be processed as one batch?"

Response - F. P. Baranowski:

Technically speaking, they cannot be, since, in the processes which we have at this time, the reagents required for their dissolution are incompatible; that is, nitric acid, in one case, or caustics, conceivably, and sulfuric acid or some other reagents in another case.

THE UNITED KINGDOM CIVIL POWER PROCESSING PROGRAMME

by

T. Tuohy, Works General Manager
Windscale Works and Calder Hall, Production Group
United Kingdom Atomic Energy Authority

AEC Note

The Windscale Works and Calder Hall are adjacent to each other and are both located at Sellafield, Calderbridge, Cumberland. The principal Windscale facilities are:

Principal AEA chemical processing plant; AGR; HERO (AGR type, full-scale heated critical facility soon to be constructed); new plutonium separation plant scheduled for construction; laboratory facilities for study of irradiated materials, heat transfer, fluid dynamics, separation processes, reactor physics, biological uptake of radionuclides, and metallurgical examination of highly active fuel elements. Windscale I and II reactors (abandoned).

The principal Calder Hall facilities are:

Calder 'A' and 'B' stations, each having two approximately 200 MW (maximum thermal), 37 MW (maximum net electrical), combined power/plutonium producing reactors. Power produced is sold to CEGB and distributed over national grid.

Before I start, I would like to introduce Ken Saddington, Head of Development and Engineering at Windscale, who came along with me to this processing symposium. Ken has been in this business for a long time and I am sure that most of you know him personally or by reputation.

I have had a few invitations recently to address groups at dinner and was beginning to think that because of my initials, T. T., I was being mistaken for Tommy Tucker. As you know, Tommy became famous for his singing. You can imagine my concern when notified that T. T. had been selected to honor the "purge-request" which the Authority had received from your AEC. I was greatly relieved to find that instead of a "p-u-r-g-e - request" it was a "P-e-r-g-e - request" and that it was from Alex Perge, spelled P-E-R-G-E, of the US-AEC requesting a UK representative to present the Authority's plans for civil reactor spent fuel reprocessing. Since that is the prime reason for my being here, it is time to present the Authority's program. I guess I really should have said - "start to sing".

INTRODUCTION

As the chemical processing programme in the United Kingdom must depend upon the number of reactors in operation by a given date, it would seem to be appropriate, as an introduction to the processing programme, first to consider the programme for the provision of nuclear power stations, and also to consider the part to be played in this programme by the Atomic Energy Authority.

The initial proposals for the Nuclear Power Programme were set out in a Government White Paper in February, 1955, and this programme aimed at the provision of 12 nuclear power stations using natural uranium fuelled graphite moderated and carbon dioxide cooled reactors, with a total output of 1500-2000 megawatts, to be in operation by 1965. Technical advances particularly in the welding of the thick steel plate needed for pressure vessel construction indicated that whereas in the Calder Hall reactors two inch thick steel plate was the maximum that could be used, the first nuclear stations to be built for the Electricity Authority could be constructed using three inch thick steel plate for the pressure vessel. This permitted an increase in the size of the reactor, and in the operating pressures and temperatures. Reactors with a larger net electrical power output could therefore be constructed, and an amended programme was announced in March, 1957, giving a total electrical output of between 5000 and 6000 megawatts by the end of 1965. The programme was reviewed in October, 1957, leading to a postponement of one year in the achievement of the output of 5000 to 6000 megawatts.

In implementation of this programme five nuclear power stations are already under construction with a net electrical output of 1900 megawatts and two others with a net electrical output of 1100 megawatts are at the planning stage. Two of these stations will be in full operation by 1962 and three others by 1963.

Although the nuclear power stations will be owned and operated by the Electricity Authority, the Atomic Energy Authority has several responsibilities in the implementation of the overall programme.

Firstly, the Authority is carrying out an extensive research and development programme into the more advanced systems to be used in the nuclear power stations of the future.

Secondly, it is responsible for the procurement of the materials necessary to produce nuclear fuel, and for the production of the fuel elements.

Thirdly, the Authority is responsible for the chemical processing of the irradiated fuel arising from the power programme.

In order to meet this third commitment the Atomic Energy Authority is at present designing a new chemical separation plant which is scheduled to be in operation in 1963.

The design of the nuclear power stations is such that the reactors will charge and discharge fuel whilst operating. This is different from the Calder Hall reactors in which it is necessary to shut down the reactor and release the gas pressure in order to discharge.

The aim in the nuclear power stations is to achieve an irradiation of 3000 MWD/T. As the reactors will be charged and discharged whilst operating, it will be necessary to discharge some fuel at low irradiation in the first instance in order to establish a cycle such that all fuel can ultimately be discharged at 3000 MWD/T. Some irradiated fuel from the power programme will, therefore, become available for chemical processing in 1962, and the quantity available will build up to between 500 and 1000 ton. by 1965. Subsequent build-up will necessitate the construction of a further chemical processing plant so that it is available for operation in 1966.

FUEL HANDLING

Each nuclear power station will have associated with it a cooling pond in which the fuel will stay for 40 days in order to allow short-lived activity to decay and therefore reduce the amount of shielding necessary on the transit containers. The containers will weigh 50 tons each containing two tons of fuel and will be shipped by rail to Windscale Works in Cumberland, the existing chemical processing site. Here the transit containers will be unloaded in a shielded cell and by means of mechanical equipment operating under water the cladding material will be stripped from the fuel elements. Although the design of fuel

elements in each nuclear power station is different, all have a simple geometry and the uranium fuel is in all cases a simple cylindrical rod slightly larger than one inch diameter and varying in length from 20 inches to 40 inches. With this simple geometry mechanical decanning is a practical proposition, and the process to be used is to force the fuel element past three spring loaded cutting wheels set at 120°, the cut being made such that the can wall is just not penetrated. Three ploughs then follow up and effectively peel off the can similar to peeling the skin off a banana. The decanned rods will be transferred to transit containers still under water and then fed by internal electrical truck to the chemical plant.

The water from the decanning plant will be circulated through a filter to remove suspended solids, and periodically will be discharged to an evaporation plant where the accumulated activity will be concentrated to small volume and stored in stainless steel tanks.

There is considerable advantage in using mechanical decanning if the fuel element has simple geometry, as a dissolution process to remove the canning material gives rise to an additional medium active liquor to be disposed of.

EXISTING CHEMICAL PLANT

The existing chemical plant at Windscale was designed to deal with the output of the two original air cooled reactors which were also situated at Windscale. This plant has since been modified such that it can now process all the irradiated fuel arising from the eight Calder Hall type reactors, six of which are already in operation, one being commissioned at present, and the remaining reactor to be commissioned early next year.

The process involves the use of four separate plant units covering the following stages in the process:-

- a) Primary Separation in which the bulk of the fission products are removed at the first stage of the process, and the initial separation of plutonium is made from the uranium.
- b) A Uranium Purification Plant to remove the last remaining traces of fission products and plutonium and produce a pure uranyl nitrate.
- c) A Plutonium Purification Plant to carry out the final separation of plutonium from the uranium and remove residual fission products.

d) A Plutonium Metal Production Plant.

The plant will not be utilized to its full capacity in 1962, and it is likely that the first fuel arising from the Civil Power Programme will be processed through the existing plant.

PRIMARY SEPARATION PLANT

The existing separation plant was designed such that the highly active sections could be operated for ten years without any maintenance. Towards this end, the contactors used were kept as simple as possible and packed columns were used. The whole plant was constructed in stainless steel and was welded throughout, each weld being made to the highest possible specification and radiographed. No pumps or mechanical equipment were incorporated in the plant inside the biological shield, and the flow of liquids through the plant is by gravity. Using gravity flow and packed columns necessitates the use of a very tall building and it is in fact 200 feet high, and has on top a chimney which discharges at a total height of 400 feet. The attempt to design a plant which would not be maintained for a period of ten years, was not entirely successful, but seven years trouble free operation of the plant within the biological shield was achieved before a weld failure occurred. This failure arose at a point in the plant which was not thought to be subject to corrosive liquids, and the single weld concerned had not been radiographed.

The solvent used in this process is butex, known as dibutyl carbitol in the United States, and five columns are employed. The irradiated fuel is first dissolved in nitric acid, and after cooling and adjustment of acidity is fed to the first column, in which the bulk of the fission products remain in the aqueous phase whilst the uranium and plutonium pass into the solvent phase. The plutonium is reduced using ferrous sulphamate before passing into the second column in which the plutonium passes into the aqueous phase leaving uranium in the solvent. In the third column the uranium is washed out of the solvent using dilute acid, and the uranyl nitrate solution is passed to the Uranium Purification Plant for further treatment. The plutonium solution is re-oxidized using sodium dichromate and is taken back into the solvent in the fourth column and is backwashed into the aqueous phase in the fifth column, the resultant solution being evaporated prior to transfer to the Plutonium Purification Plant. The uranium solution arising from the primary separation process is given a further treatment using butex as solvent, but as the levels of activity are very considerably reduced, the type of contactor used is a stirred mixer settler.

The plutonium solution from the Primary Separation Plant is

purified using pulsed column contactors, with 20% TBP/Odourless Kerosene as the solvent to give a pure solution of plutonyl nitrate.

The plutonyl nitrate is evaporated, the plutonium precipitated as exalate, the exalate heated to produce oxide which is fluorinated with anhydrous hydrofluoric acid, and finally reduced to plutonium metal by heating in a reaction vessel with calcium.

This process has two major disadvantages. Ruthenium, one of the major fission products, is partially extracted into butex in the first column in the primary separation process, and this eventually gives rise to fairly large volumes of active waste solution. These solutions are stored in stainless steel tanks for a period of two years to allow radioactive decay before feeding to an effluent treatment process prior to discharge to sea via a pipe line of which the outlet is two miles off-shore. Also, it is necessary in the later stages of the process to use concentrated ammonium nitrate solution as a salting out agent, and the ammonium nitrate appears in the waste stream containing ruthenium and renders high concentration by evaporation impossible.

PROPOSED NEW CHEMICAL PLANT

In view of experience gained in the operation of mixer settler type contactors in the processing of medium active materials, and experience gained in the decontamination of highly active plant, the type of contactor to be used throughout the proposed plant will be multi-stage box type mixer settlers, each mixing compartment being mechanically agitated by an individually driven paddle type stirrer. Facilities will be built into the plant for remote de-sludging of the contactors. The whole plant will be constructed in stainless steel, and for the highly active sections, the original principle of designing a plant which will not need maintenance within the biological shield for a number of years, will be adhered to. Standby capacity will be provided at the highly active stages so that operations will not be held up should it be necessary to enter a highly active cell to carry out maintenance.

The solvent to be used throughout the whole process is 20% TBP/Odourless Kerosene. Using this solvent it is hoped to achieve an overall fission product decontamination factor of 99.98% in the initial extraction as compared with approximately 99% in the existing butex process. As salting out agents will not be used, low active waste streams can be concentrated by evaporation, the nitric acid arising from the evaporation process being recovered and re-used.

The decanned fuel will be dissolved continuously in nitric acid, the dissolving system incorporating a condenser and acid

scrubber. Dilute nitric acid fed to the scrubber passes counter current to the nitrous fume evolved in dissolution, and an oxygen feed re-oxidizes these fumes to nitric acid which is absorbed by the dilute nitric acid feed. The gases ultimately leaving the dissolver system pass through a caustic scrubber before venting to atmosphere through a filter. The uranium and plutonium are extracted into T.B.P using two cycles, the first of which removes 99.9% of the fission products in the aqueous phase, and the second of which removes 80% of the remaining fission products giving the over-all decontamination factor of 99.98%. The fission product solution is evaporated by a factor of about 100 and the concentrate is stored in stainless steel water cooled tanks. In the second contactor the uranium and plutonium are separated by using a reducing strip of ferrous sulphamate which takes the plutonium into the aqueous phase. The anticipated efficiency of separation of plutonium from uranium is 99.99%.

The uranium solution is given a further solvent extraction cycle to remove the last traces of plutonium and fission products, and the resultant pure solution of uranyl nitrate is evaporated and then converted to oxide by thermal de-nitration using fluidized bed technique.

The plutonium is oxidized using sodium nitrate and undergoes two further extraction cycles to give a product of pure plutonyl nitrate which is converted to metal via the tetrafluoride and calcium route.

Used solvent is recovered by washing successively with water, sodium carbonate, caustic soda, and dilute nitric acid.

Apart from the highly active fission product effluent which is evaporated and stored, three other effluent streams arise:-

- a) Nitric acid containing tons of curies per cubic metre arises from the second extraction cycle and from the uranium purification cycle. These solutions are evaporated in a two-stage evaporator, the concentrate being cycled to the highly active evaporator, and nitric acid being recovered from the distillate, which is passed to a counter current bubble cap concentration tower to produce acid at either six or twelve normal.
- b) Sodium carbonate wash-liquors arising from solvent purification are evaporated by a factor of five and passed to delay storage for a period of four years to allow ruthenium, zirconium and niobium to decay. The solution is then passed through an ion exchange column to recover remaining traces of plutonium before being discharged to sea.

- c) Low active effluent containing traces of fission product activity arise from the solvent washing process, and these are discharged direct to sea. The total discharge to sea amounts to about 20 curies per day of which the largest fission product constituent is ruthenium.

The plant is divided into a number of concrete cells as follows:

- a) A highly active cell which contains the dissolver and the first contactor.
- b) A medium active cell which contains the contactors used in the second purification cycle and the washing plant for the more highly active solvent.
- c) A uranium purification cell.
- d) A plutonium purification cell.
- e) A solvent washing cell.

The ratio of fission product activity levels in these cells taking the highly active cell at an arbitrary figure of one million is as follows:-

Highly active	-	1,000,000
Medium active	-	100
Uranium purification	-	5
Plutonium purification	-	Less than 1
Solvent washing	-	200

VENTILATION

The ventilation system is arranged such that air flows from the operating area into the cells, the ventilation of the plutonium and uranium sections being kept separate. Air extracted from the cells is filtered before passing to atmosphere via a chimney.

In addition all vessels within the biological shield are connected to a ventilation manifold, air being drawn from the cells into the vessels and via the manifold to a packed water scrubber followed by a filter before discharge through the chimney to atmosphere. Where equipment pierces the biological shield there is either a positive seal or an air flow of three feet per

second through the gap.

FIRE PRECAUTION

For the purpose of fire precaution each cell is considered as a separate entity. No inflammable material is used in the construction of the cell and plant and electrical equipment located within the cell is flame proofed and retractable from outside the cell. Fire control is achieved by the use of carbon dioxide as smothering gas which is stored in liquid form at high pressure in a separate building. An installed pipe system distributes the gas to the cells in sufficient quantity to extinguish any fire. The release system is coupled to a detection system which automatically releases the gas to the affected cell. The automatic system also operates dampers to divert the exhaust from the cell to a clean bank of incombustible absolute filters located in a shielded cell.

Conventional installed foam systems for dealing with solvent fires are used augmented by portable fire extinguishers in the inactive areas of the plant.

This, in brief, is the outline of the UK Atomic Energy Authority plan and plant for chemical processing of civil power reactor fuels.

For the UK Atomic Energy Authority and also for Mr. Saddington and myself, I again would like to thank Alex Perge (spelled P-E-R-G-E) and the AEC for inviting us to participate in this meeting.

Thank you.

EUROCHEMIC, ITS HISTORY AND PROGRAM

by

E. Detilleux
Study & Research Office
Eurochemic Company, ENA, OEEC

I have been asked by Mr. Perge, of the AEC, to give you, this evening, a short description of the history of the Eurochemic Company and of the work achieved up to-day by this recently created organization.

HISTORY

About three years ago, the European Nuclear Agency, which is the atomic-branch of the European Organization for Economical Cooperation (O.E.E.C.) investigated the needs and interests of its members in the field of nuclear fuel processing.

In the beginning of 1957, it appeared that 12 countries were interested into this project. These nations were: Austria, Belgium, Denmark, France, West Germany, Italy, Netherlands, Norway, Portugal, Sweden, Switzerland and Turkey. More recently, Spain joined this group.

An agreement was proposed in March 1958, indicating that the plant capacity should be 100 T/year of different types of fuels from natural up to 5% enrichment and that the plant should be located at Mol, Belgium, on a proposed site joining the Belgian Nuclear Laboratories.

Before the official foundation of the Eurochemic company, the ratification of the Parliaments was required which is normally obtained, after a lot of time only. In order to start immediately the design of the project, the Nuclear Agency decided to set up a provisional organization with a limited staff. This organization, called Eurochemic Research and Study Office, started its work at Mol in April 1958. It prepared the first design of the 100 T/year plant and started an experimental program in close relation to the

project.

In April of this year, the Management Committee of Eurochemic, decided to change considerably the first concept of a 100 T/year plant. It decided to consider a pilot plant where special emphasis should be placed on research and development character. The capacity was fixed at 350 Kg U/day without any consideration on the yearly capacity.

Since this decision, the Study and Research Office is working on this new project which will be explained briefly hereafter.

The ratification of the 1958 agreement has been obtained in July of this year and the Eurochemic company has been immediately created. The funds will be brought partly by the 13 Governments, partly by the industry of the member-countries.

At the present time, the Company is in organization and the final contracts with the architect-engineers in charge of the construction of the laboratories and plant should be signed within the 2 next months.

As far as we know to-day, the laboratories should be completed at the end of 1962 and the plant in 1963.

THE SITE

The selected site is a ground of one square Km located just North of the Belgian Nuclear Research facilities at Mol, fifty miles North of Brussels.

It is undoubtful that this site presents some disadvantages. I mention especially the relatively high density of population : we have around 30,000 inhabitants in a circle of 5 km in diameter, and the presence of the water table at 2 m under the surface.

This selection, however, allows to operate in community with the Belgian Center some expensive facilities like the waste treatment, site radioactive survey, etc. Moreover, Eurochemic work could immediately be started by renting office and laboratory space from the Belgian organization.

THE ELEMENTS

The information received at the present time about the fuel element characteristics are still incomplete. However, from the existing information, we can group the elements to be processed into the following categories:

- 1° Canning materials : Al, Mg, Zr, SS
- 2° Core materials : U metal, UO_2 , U-Mo, U-Zr
- 3° Enrichment : from natural up to 5%
- 4° Structures : from simple slugs to PWR or BWR assemblies

THE PROCESS

The plant will be directly maintained. It will use 30% TBP in hydrocarbon diluant and pulsed columns as contactors. Now we could review rapidly the different steps of the process outlining the particularities of the project.

1. Head End

At the beginning, Eurochemic does not intend any kind of mechanical decladding except some mechanical preparations such as inert parts cutting or dismantling.

The head end facility should be essentially composed of two dissolvers: one conventional batch dissolver and one geometrically safe batch dissolver.

The proposed decladding procedures are: Caustic decanning for aluminum clad material, Sulfex Process for SS, Zirflex process for Zircalloy 2, dilute sulfuric or nitric acid for magnesium.

The conventional dissolver should be made of SS and the geometrically safe one of a material suitable for sulfuric acid and Zirflex decladding mixture, for instance Nionel or Hastelloy F.

2. The extraction

The proposed extraction flowsheet is a 2 cycles Purex:

- one first cycle for codecontamination and partition of uranium and plutonium, and
- two second cycles for a further purification of uranium and plutonium respectively.

A particularity of the proposed flowsheet is the use of a dilute feed in the first cycle; 140 gr U/liter. This is proposed to allow the adjustment of the 5% enriched solutions without using geometrically safe tanks for this operation, the core solution being, before transfer, diluted in the safe dissolver to achieve an uranium concentration well below the critical concentration

for 5% enriched uranium.

The concentrations in the second cycles are the concentrations of a standard Purex-flowsheet, the geometrically safe first cycle evaporator being used for the concentration.

Moreover, to decrease as much as possible the volumes of low level effluents, we propose to backcycle into the stripping columns the slightly contaminated water resulting from the cycle evaporators. For the same reason, the aqueous phases from the extraction columns of the second cycles will be backcycled into the extraction column of the first cycle after appropriate concentration.

A dual temperature scrub is also proposed to increase the decontamination factors achieved in the extraction columns.

3. The final purifications

The uranium final purification will be carried out on conventional silica-gel columns.

The plutonium product will be purified on fixed beds of anionic resins, but the use of continuous exchangers of Higgins type is also considered.

The specifications concerning the chemical state and the purity of the final products have not yet been well determined.

4. Solvent recovery

The used solvent of the first cycle will be treated separately from the solvent of the second cycle.

A sodium carbonate wash is foreseen in both cases, eventually with potassium permanganate addition in the case of the first cycle TBP. This treatment will probably be followed by an acid wash and a new alkaline wash.

Turbo-mixer contactors are proposed (single stage mixer-settler) for this purification.

5. The waste treatment

The location of Eurochemic site imposes very strong restrictions for the disposal of the liquid effluents. Indeed, a lot of farmers dispersed around the site use the ground water as drinking water and the Belgian regulations do not allow a discharge exceeding 50 millicuries per day in the closest river, i.e. the Mol-Nethe.

Our radioactive effluents have been divided into three main categories :

1. the high level waste : principally the first column raffinate will be evaporated and stored in acid form in two 30,000 gallons stainless steel tanks. This storage capacity will be sufficient for about 4 years of operation;
2. the intermediate level waste : containing the decladding and decontamination solutions from the plant will be concentrated if possible and stored in neutral conditions;
3. the low level waste : will be sent by pipeline to the waste treatment facility of the Belgian Nuclear Laboratories for chemical treatment and discharge in the river.

If necessary, the condensates from the waste evaporators could be processed by the ions exchange columns normally used for the purification of the water of the storage pond.

ESTIMATION OF INVESTMENT COST

A quite recent estimation based on the actual Eurochemic project and on the labor cost in Europe indicated that the 350 Kg/day processing plant would cost 20 millions dollars, 12 millions being invested in the main process building and equipment.

The same study indicated that a plant of 1 T/day capacity would cost 25 million dollars.

I cannot conclude this short review about Eurochemic without mentioning that the work of the Study and Research Office has been performed not only by a close cooperation of the representatives of the member-countries, but also by a very efficient assistance program elaborated by the U. S. Atomic Energy Commission.

This program includes especially :

- the presence at Mol, since one year, of a highly qualified advisor
- the exchange and gathering of information,
- and finally, during these last three weeks, the opportunity for members of Eurochemic to visit three processing plants of this country and discuss with their personnel the Eurochemic projects.

I am the interpreter of my colleagues telling you how we appreciate your help and how we are satisfied for the kindness and invaluable help we got from the people we met during this tour.

PROCESSING POWER FUELS AT THE SAVANNAH RIVER PLANT

By H. L. Hull

E. I. du Pont de Nemours and Company
Wilmington, Delaware

ABSTRACT

Plans are being made to process fuels from Chalk River, Canada and Lagoona Beach, Michigan at the Savannah River Plant. A series of three papers, introduced by this one, describe the plans in detail.

DISCUSSION

Under the Interim Processing Program of the Production Division of the U. S. Atomic Energy Commission, core fuel from the Enrico Fermi Atomic Power Plant and fuel from the Canadian NRU and NRX reactors are to be sent to the Savannah River Plant for processing.

It is planned that a portion of existing facilities be used part time in order that processing costs be held to a minimum. Some modifications will be required; however, the cost of these modifications will be considerably less than the cost of providing a new plant.

The schemes for processing these fuels differ in a number of respects from schemes that might be selected for a new plant, because they have to be compatible with existing stainless steel equipment. This places limitations on volumes, concentrations, chemicals, temperatures, and type of process selected. The use of existing large equipment means that nuclear safety will be maintained by keeping fissionable materials at low concentrations.

The times at which the fuels are processed will depend on availability of the equipment from its normal functions, availability of sufficient fuel to justify the expense of switching from one fuel to another, and on the decay of radioactive iodine.

The nuclear reactor at the Enrico Fermi Atomic Power Plant was designed by Atomic Power Development Associates. The nuclear reactor was built and will be operated by the Power Reactor Development Company. Core fuel from this reactor is known as PRDC core fuel. The turbine and electric portion of the plant will be built and operated by the Detroit Edison Company.

The Enrico Fermi reactor is expected to go critical in about a year and is to operate about two years on two cores of the original design and then switch to a radically different design of core fuel. It is to be more than three years before all of the original type core fuel is ready for processing. Research for processing the original design began about two years ago and was carried out at Brookhaven National Laboratory, Oak Ridge National Laboratory, Savannah River Laboratory, and the du Pont Engineering Research Laboratory, Wilmington, Delaware. Processing plans are in preliminary stages prior to engineering design. Research has not yet started on processing core three design.

The Canadian NRU and NRX reactors have been in operation for some time. In the past fuel from the NRX reactor was cut into short lengths at Chalk River and shipped to Oak Ridge National Laboratory and to Hanford for processing. Currently fuel from these reactors is being shipped to the Savannah River Plant where it will be chemically processed without cutting. Special equipment has been designed and procured for chemically processing these fuels, but it has not yet been installed.

John Langhaar will tell us about shipping, receiving, storage, and mechanical treatment of PRDC core fuel and Canadian NRU and NRX reactor fuel at the Savannah River Plant.

MECHANICAL HANDLING OF CHALK RIVER AND PRDC FUEL

By J. W. Langhaar

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ABSTRACT

NRU and NRX fuel from the reactors at Chalk River, Ontario, is shipped to the Savannah River Plant in a finned, externally air-cooled cask provided for this purpose. The cask has an internal length of 11 feet to accommodate full-length elements. At SRP the elements are placed in a dissolvable frame or "bundle", about 25 per bundle, for storage and subsequent handling. Two bundles at a time are shipped from storage to the separations plant in an available 70-ton cask which has been equipped with a suitable internal rack.

It is planned to ship at least the first two charges of PRDC fuel to the Savannah River Plant. The blanket element end sections of the fuel assembly will have been removed at the reactor site. Criticality hazards will probably limit handling operations to four fuel assemblies in any basket or bundle. The shipping cask design has not yet been specified. The possible need for removing the stainless steel housing tube before processing is to be determined by studies of dissolver operation.

DISCUSSION

Irradiated fuel from two reactors at Chalk River, Ontario, is now being shipped to the Savannah River Plant for processing, and it is expected that the initial charges of fuel from the PRDC reactor at Detroit will be processed at the Savannah River Plant. The present discussion outlines the procedures and facilities for shipping the fuel and for packaging it preparatory to dissolving. As with most engineering problems, a wide variety of alternative solutions appeared technically feasible, and I shall indicate in a general way the reasons for the final selection.

The two types of Chalk River fuel are designated as NRX and NRU. The NRX element consists of a rod of natural uranium about 10 feet long and 1.4 inches in diameter, clad with aluminum. The NRU element consists of five flat plates of natural uranium about 10 feet long, individually clad with aluminum and contained within an aluminum housing tube of 2 1/2 inches diameter. Each type of element contains 120 pounds of uranium.

For many years NRX fuel was chopped into short pieces at Chalk River and shipped in small casks to Oak Ridge, and more recently to Hanford for processing. Two to three years ago, when plans were being developed for shipping fuel from the NRU reactor, which was not yet in operation, one of the questions was whether similar handling methods would be acceptable. The severe contamination problems encountered at Chalk River and at various USAEC facilities when handling irradiated natural uranium exposed directly to water led to the decision that the added investment for handling and processing full-length fuel was well justified. The magnitude of the contamination problem is indicated by experience that respiratory equipment is commonly required for persons working around water whose activity exceeds about 10^{-8} curies/ml. of long life fission product. This corresponds to about one gram of uranium in 5000 gallons of water in the case of NRU fuel.

The nature of the dissolving facilities, which will be described by Dr. Hull, dictated that the fuel be packaged in a dissolvable container of such type that some reasonable number of elements could be charged vertically in a single operation. The package, or bundle, designed for this purpose is shown in Figure 1. The size of bundle was determined by certain dissolver limitations and by the load carrying capacity of monorail equipment in existing SRP disassembly basins. A bundle normally contains about 25 NRU elements, and because of weight limitations only about 25 of the smaller diameter NRX elements are put into a bundle.

The type of cask selected was an externally-finned, air-cooled design similar to the 70-ton casks which are described in detail in the AEC Research and Development Report DP-357. Figures 2 and 3 are pictures of the 70-ton cask and the Chalk River cask respectively. The subject of acceptable methods of heat removal from a cask has been debated extensively within the various organizations concerned with design and operation of such equipment. In the absence of adequate data concerning the reliability of various methods and the damage resulting from loss of cooling, the tendency of AEC facilities has been to adopt the viewpoint that fuel or cladding should not melt even if all water should be lost and mechanical contrivances should fail. As some of you are aware, studies are in progress to try to put such decisions on firmer ground.

Fig. 1—Bundle for Chalk River elements.

Fig. 2—70-ton cask.

Fig. 3a—Chalk River cask and cradle, side view.

Fig. 3b—Chalk River cask and cradle, perspective.

In the case of the Chalk River cask the maximum quantity of fuel in the cask is determined not by heat dissipation capacity, but rather by physical dimensions of the cask to stay within the 55-ton load limit for the Chalk River crane.

Some consideration was given to bundling the fuel at Chalk River. This was concluded to be uneconomical because the cask capacity would thereby be reduced by a factor of about two.

The method of loading the cask with NRU elements at Chalk River consists of preloading 120 to 140 elements in a basket containing two loose stainless steel straps, so that the entire load may then be lifted by these straps and placed in the cask, which rests on an underwater platform.

The method of unloading the cask at SRP is shown in Figure 4. The same method is used for small casks at Hanford, Idaho Falls, and Savannah River, and for large casks at Idaho Falls. As you will note, the lid is supported by underwater beams while the cask body is moved laterally in such a way as to expose the cask cavity. The 18 foot crane hook spacing, originally provided for the 70-ton casks, is too great for the Chalk River cask. An ordinary load-bar type of yoke cannot be used because of interference by the lid supporting structure. Consequently a carbon steel cradle was constructed, with suitable trunnion spacing, as shown in Figure 5. The cask rests in the cradle during handling at SRP, but the cradle remains on the railroad car at Chalk River.

The method of fastening the cask to the cradle and the cradle to the car is sometimes called a "floating load" design. The cask is subject to wide temperature variation, such that precaution must be taken to avoid excessive stresses from thermal expansion. Holddown bolts through the feet of the cask are provided with sufficient clearance so that the cask may move vertically about 1/8", and horizontally a small amount within the confines of end bumpers and side bumpers. Through-bolts could be used for the cradle-to-car fastening, but appear to have no advantage. Recent experience has indicated that high sidewise as well as endwise shock may occur during shipment, and that side bumpers should be designed for shock loads of several g. Steps are being taken to equip one or more shipments with shock recording equipment.

Alongside the cask in the transfer pit is a bundle loading spot. NRU elements are removed from the cask one at a time by means of a single point pickup tong suspended from a monorail crane, and transferred to the bundle. The locking bars on top of the bundle are swung shut and locked in place. A 3-ton multiple-trolley hoist then carries the bundle over the fixed monorail system to a swimming pool type of storage. No disassembly or cutting of the assemblies is required at SRP, since the end fittings are sawed off at Chalk River

Fig. 4—SRP cask transfer pit.

Fig. 5—Cradle for Chalk River cask.

and the elements as shipped are dissolvable.

No NRX shipment has yet been received at SRP. The plan for these elements is to bundle them into groups of 25 elements at Chalk River, by means of two aluminum straps or cables, and to load them into the cask in this fashion. A group may then be transferred as a unit from the cask to a bundle, in view of the fact that weight limitations permit a bundle to be physically only about half full of NRX elements.

The bundles are too long to fit in the Chalk River cask, which has an internal length of 11 feet. One of the 70-ton casks has been equipped with an internal rack or fixture to accommodate two bundles, and in this way the elements are transferred to the processing area.

Existing facilities for unloading and storing fuel are not equipped to contain safely or dispose of large amounts of radioactive contamination. It is therefore important to avoid shipping an unprotected failed element, since the corrosion rate of plain uranium in water is rather high and the cask water temperature may be as high as 90°C. The current acceptance sampling procedure involves recirculating the cask water at the rate of about 10 gpm, using the two diagonally opposite drain pipes, and sampling this water at intervals for four days. The initial activity, rate of increase, and gamma spectrum are considered in concluding whether or not a failure is present. The plan is to encapsulate all failed elements in suitable aluminum containers before shipment. The container has a tight-fitting cap incorporating a filter which will permit escape of gas but retain particulate matter. There is some possibility of a failure occurring or becoming active during shipment. In this case costly special procedures, perhaps involving considerable delay, would be required to unload and store the fuel.

Decontamination of stainless steel casks of this type, with a sandblasted finish, has normally been fairly easy when the transfer pit water has been maintained at activity levels of less than 10^{-10} curies/ml. On one occasion when the water activity reached about 10^{-8} curies/ml, decontamination to an acceptable level for unescorted shipment was difficult, and required more than two days of scrubbing. The relative merits of a plain stainless surface vs. a painted surface under such conditions have not been thoroughly evaluated, although the evidence at SRP favors the plain stainless. On one other occasion involving high activity, the cask was sprayed with a strip-pable coating before being lowered into the transfer pit. It is believed that the reduction of decontamination cost more than paid for the cost of coating. In any event, decontamination problems are an important factor in cask design and in methods of cask unloading. Simplicity and accessibility of exterior surfaces are a worthwhile objective.

The handling of PRDC fuel is somewhat in the future, and the plans may be slightly modified as studies continue. The fuel consists of 144 pins each 0.158 inches in diameter and about 32 inches long. The core of each pin is an alloy of 90% uranium and 10% molybdenum, and the cladding is zirconium. The 144 pins are tied together and maintained at proper spacing by a system of stainless steel wires. In the reactor, a stainless steel housing tube about 2 1/2 inches square inside and 8 feet long, with 1/10 inch thick walls, contains in series an assembly of blanket elements, the fuel assembly, and then more blanket elements. At the reactor site, the housing tube will be cut at two appropriate spots, so as to permit shipping the fuel to SRP and the blanket material elsewhere.

Since the PRDC fuel is of an enriched type, criticality precautions must be observed. A grid of poison plates may be used during shipment, so that each element will be individually surrounded by poison. Shipment of the fuel is to be arranged by the reactor operator. Details are not yet available but the cask should be of such type that it can be handled in an existing transfer pit. Individual baskets or containers in the cask will probably be limited to four elements each, in order that criticality hazards will not unduly complicate the handling operations. The baskets will be removed from the cask one at a time by means of a monorail hoist on the platform crane, and transferred to a bundling station where the four elements will be bound together in a single layer with stainless steel straps. Included in the bundling will be a screen or perforated plate over one end of the array and a bale at the other end for handling with a crane hook. The bundles will be stored with the elements in a vertical position in a storage rack having suitable spacing to avoid criticality.

An alternative whose need is to be determined by dissolving studies involves removal of the housing tube. In this case four of the pin assemblies without housing would be placed in a basket or bundle whose design would be determined by dissolver requirements. We suspect that dimensional changes during irradiation and storage would prevent removal of the fuel from the housing by ordinary pushing or pulling techniques, and that slitting of the housing would be required. For this purpose we visualize an underwater device which would feed the assembly between two milling cutters rotating about vertical axes and located so as to cut the housing lengthwise at two diagonally opposite corners. A machine for this specific application has not yet been designed and we hope that it will not be needed; however the principles involved have been applied in other underwater equipment. A cutting operation of this type would preferably be done in an isolated tank or basin equipped with facilities such as filters and deionizers for collecting and disposing of activity.

Fig 6—LMF cask

As with Chalk River fuel, it is expected that known failures of PRDC fuel will, before shipment, be placed in suitable containers.

Shipment of the bundles from the storage area to the processing plant may be done with an available 15-ton cask (Fig. 6) described in DP-357 as a "Slug Shipping Cask" and having internal dimensions of about 15" x 24" x 37" high.

CHEMICAL PROCESSING OF CHALK RIVER FUELS

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ABSTRACT

One of the existing Savannah River Plant dissolvers will be modified to accommodate eleven-foot long fuel elements from Chalk River, Canada. The aluminum cladding will be removed with sodium hydroxide, and the uranium cores will be dissolved in nitric acid. The Purex process, operated in mixer settlers, will be used to recover and decontaminate the uranium and plutonium in the core solution.

DISCUSSION

Atomic Energy of Canada Limited is shipping irradiated natural uranium fuel elements from its Chalk River site to the Savannah River Plant. There are two basic types of Chalk River fuel. The NRX reactor uses one and a half inch diameter uranium metal rods clad with aluminum. The NRU reactor uses thin uranium metal plates clad with aluminum and each group of five plates is held in an aluminum tube two and a half inches in diameter. Both types of fuel are about eleven feet long.

Existing Savannah River Plant facilities^{1,2} for processing irradiated natural uranium will be used to process Chalk River fuel except that additional fuel handling equipment will be required and a dissolver will have to be modified to accommodate long fuel elements.

The available dissolver is eight feet in diameter and eight feet tall. It is to be fitted with a special column on top (Figure 1) so that it can accommodate eleven foot fuel elements. The fuel elements will be arranged in bundles and stand on end.

Fig. 1—Dissolver column for long fuel elements.

Former practice was to saw NRX fuel under water at Chalk River so that the resulting pieces could be charged to dissolvers at Oak Ridge or Hanford. This practice has been abandoned because of the spread of radioactivity.

The aluminum cladding will be removed with a solution of sodium hydroxide and sodium nitrate.^{3,4} The aluminum solution will be stored underground in prestressed concrete tanks with steel liners. Partial recycle of the aluminum solution may be used to reduce waste volumes.

The uranium will be dissolved in nitric acid.^{3,4} Both dissolutions proceed rapidly with evolution of gases which generate foam. The maximum amount of liquid in the dissolver is limited to five or six feet to avoid excessive carry of foam to the gas handling system. Foaming during aluminum dissolution is limited by controlling the rate of addition of sodium hydroxide.

The procedure for dissolution of Chalk River fuel will consist of four steps instead of two because only half of the fuel can be immersed in solution.

The first step will be to dissolve the aluminum from the bottom half of each element and transfer the aluminum solution out of the dissolver.

The second step will consist of dissolving the exposed uranium of the bottom halves of the fuel elements. During this step, the upper halves of the fuel elements will drop into the dissolver. This solution will be transferred to an agitated tank where it will be measured and sampled.

The third step will be similar to the first step, and the fourth step will be similar to the second step.

After the fourth step, bundles of fuel will be charged to the dissolver, and the cycle of operations will be repeated. It is estimated that a complete cycle will take about three days.

Both the dissolution of aluminum and the dissolution of uranium give off large amounts of heat. This heat is removed by cooling coils in the boiling liquid and by condensers mounted above the dissolver.

Ammonia given off during aluminum dissolution is filtered, diluted with ventilation air, and sent to a 200 ft. stack. Oxides of nitrogen given off during uranium dissolution are filtered and passed through an unshielded absorber in which most of the oxides are air oxidized and recovered as nitric acid. The off-gas from the scrubber is diluted with ventilation air and sent to a 200 ft. stack.

The nitric acid solution of uranium, plutonium, fission products, and part of the aluminum will be centrifuged in a solid bowl centrifuge and passed on to solvent extraction by the Purex process.^{5,6}

The Purex process is a continuous countercurrent liquid-liquid extraction process employing tributyl phosphate as solvent and nitric acid as salting agent for the processing of irradiated uranium to separate uranium and plutonium from each other and from fission products. The Purex process can be carried out successfully in packed columns, pulsed columns, or mixer settlers. Mixer settlers^{7,8,9,10,11,12,13,14} (Figure 2) were chosen for the Savannah River Plant in order to reduce the height of building required and to minimize problems associated with changing operating conditions or starting and stopping. The particular Purex flowsheet to be used for processing Chalk River fuel in mixer settlers is given in Figure 3.

The wastes from solvent extraction will be evaporated to low volumes to reduce waste storage costs and to recover acid for reuse. The evaporator bottoms will be neutralized with an excess of sodium hydroxide. Excess sodium hydroxide is required because small amounts of organic in the wastes will be converted to carbonate acidity by radiation. The wastes will be stored underground in cooled mild steel tanks. After five to ten years, the rate of fission product heating of the waste will have fallen by a factor of ten, and it is planned to concentrate the wastes about three fold or from thirty per cent solids to seventy per cent solids. This concentrated waste will be stored in uncooled prestressed concrete tanks with steel liners and as the fission product heating rate falls the wastes will solidify.¹⁵

The solution of uranium leaving the dissolver will be analyzed to check on the amount of uranium and plutonium entering the separations plant. The analysis is difficult because of the variable complexity and high radioactivity of the solutions. Analysis of pure uranyl nitrate or plutonium nitrate solutions would be much easier.

The uranium concentration will be calculated from the nitric acid concentration, the aluminum concentration, and the density. The nitric acid concentration is determined by conductimetric analysis. Aluminum is measured by colorimetric analysis. Density is checked by the falling drop method. The calculated uranium concentration is estimated to have a precision of two per cent for ninety-five per cent confidence limits if four samples are taken and two determinations are made for each sample. The accuracy of the value of the uranium concentration is influenced by the quality of the sample and adequacy of mixing in the tank as well as by factors in the analytical laboratory. Adequate mixing is impractical in the dissolver, and a special agitated tank will be used.

Fig. 2—Three stages of a mixer-settler.

Fig. 3—Purex flowsheet for Chalk River fuel.

The plutonium concentration will be calculated from a measurement of gross alpha with corrections for uranium alpha, americium alpha, and curium alpha. This calculation requires knowledge of the specific alpha activity of the plutonium. The specific alpha activity of the plutonium can be calculated from a plutonium isotopic analysis. The precision of the value for plutonium concentration is estimated to be about the same as for uranium concentration.

The volume of the solutions will be determined to about one or two per cent by careful calibration of the tank and measurement of tank contents with pneumatic liquid level and specific gravity dip tubes.

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CHEMICAL PROCESSING OF PRDC CORE FUEL

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ABSTRACT

It is planned to process the PRDC core fuel elements in an existing stainless steel dissolver at the Savannah River Plant. The zirconium cladding will be dissolved in dilute hydrofluoric acid. The uranium-molybdenum alloy will be dissolved in nitric acid. Stainless steel portions of the fuel assemblies will be retrieved and buried. Chain nuclear fission will be avoided by keeping the uranium at low concentrations in solution and by handling the fuel in thin slabs.

DISCUSSION

The Power Reactor Development Company will separate the core fuel from the blanket fuel and begin to ship core fuel in about a year and a half. The last of this type core fuel should arrive at the Savannah River Plant in about three years.

Each of the first two PRDC cores will consist of ninety-one sub-assemblies and each subassembly will contain 144 fuel pins. Figures 1 and 2 show a subassembly. Each pin is 0.158 inches in diameter and about thirty-two inches long. The active portion of the pins is an alloy of 10% molybdenum and 90% uranium. The uranium is 25.6% uranium-235. The cladding of the pins is five mils of reactor grade zirconium. The pins of each subassembly are kept separate by means of wire and locking bars. The wire and locking bars make up a unit known as a bird cage. The bird cages are made of Type 347 stainless steel.

Processing this fuel is a special problem. Stainless steel and zirconium are combined in the same fuel. It is planned to retrieve the stainless steel bird cages from the dissolver because it is not feasible to chemically dissolve them in the available dissolver of Type 309 SCb stainless steel. It would be extremely difficult to mechanically separate the locking bars from the fixed end caps on

Fig. 1—PRDC core fuel subassembly.

Fig. 2—PRDC core fuel subassembly pin arrangement details.

each pin. A late design change substituted zirconium for stainless steel in making the fixed end caps. This will make it easier to obtain complete dissolution of the material encased by the fixed end caps.

The fuel is used in a fast reactor and has a strong tendency toward criticality in light water. Four subassemblies will be placed in a perforated stainless steel basket. The basket will be lowered into the dissolver. Chain nuclear fission will be avoided in the dissolver because the basket will keep the pins in a thin slab until they are dissolved.

The research and development for chemical processing of the first two PRDC cores is summarized in Brookhaven National Laboratory reports^{1,2} and in Savannah River Laboratory reports.^{3,4,5,6,7,8,9,10}

The reactor grade zirconium cladding will be dissolved in boiling 0.075M HF according to the following chemical equation:

About five hours will be allowed for this reaction. At this time nearly all of the cladding will be dissolved, but some of the zirconium end caps will remain.

Aluminum nitrate solution will be added to give about one atom of aluminum for each atom of fluoride. Nitric acid will be added to make the dissolver solution 3M HNO₃. The aluminum nitrate was found to be necessary to avoid rapid corrosion of the dissolver welds.

The uranium-molybdenum alloy dissolves readily in boiling 3M HNO₃ and will be nearly all gone in about ten hours. Reaction products are oxides of nitrogen, uranyl nitrate, and Mo(VI). Small amounts of solids have been found in the resulting solutions. Tests show that the solids are mostly zirconium and molybdenum and that they contain less than 0.1% of the uranium.

There will be four locations within the dissolver for baskets of fuel. A single basket containing four core subassemblies will be lowered into the dissolver for each cycle of HF and HNO₃. Complete dissolution of zirconium and uranium-molybdenum alloy will be assured by leaving each basket in the dissolver for four cycles of HF and nitric acid. The first basket will be retrieved immediately before the fifth basket is placed in the dissolver. Similarly, the second basket will be removed before placing the sixth basket in the dissolver.

About 2200 gallons of liquid will be used in the dissolver for four core subassemblies. The solution leaving the dissolver will contain about nine grams total uranium per liter. It will be stirred and sampled to determine the quantities of material entering the plant. The solution will be centrifuged to remove solids prior to solvent extraction.

Fig. 3—SRP flowsheet for PRDC core fuel.

The solvent extraction will be carried out in mixer settlers. The solvent extraction flowsheet is shown in Figure 3. Some modifications to this flowsheet should be expected.

The clarified dissolver solution will be fed to the middle of the first mixer settler. Four hundred volumes of 10% tributyl phosphate in kerosene will be used as solvent for each 100 volumes of feed. Fifty volumes of 3M HNO_3 will be used as scrub.

Uranium and plutonium will come out of this mixer settler in the product solvent stream. Zirconium, molybdenum, aluminum, fluoride, and fission products will go out in the aqueous waste stream.

The second mixer settler will be used to separate uranium from plutonium. Seventy-five volumes of 0.1N nitric acid - 0.04M ferrous sulfamate will be used to strip the plutonium from the solvent stream, and 170 volumes of 10% tributyl phosphate in kerosene will be used to keep the uranium out of the aqueous plutonium product stream.

The third mixer settler will use 500 volumes of 0.01M HNO_3 to strip the uranium from the organic solvent stream.

The aqueous uranium stream and the aqueous plutonium stream will be processed through an additional cycle of solvent extraction for further purification from fission products.

The aqueous waste stream will be neutralized and evaporated to give about five hundred gallons of waste per subassembly. This waste will be stored in mild steel tanks with cooling coils. The processing of two reactor cores from the first two years of reactor operation will result in about 100,000 gallons of waste. After the fission products have decayed five to ten years, it is planned to concentrate the wastes about three fold, resulting in about 35,000 gallons for final storage. As has been noted previously,^{11,12} the cost of waste storage is not likely to be a significant item in the cost of nuclear power.

The analytical and measurement problems for PRDC core fuel have not been studied as thoroughly as for the Chalk River fuel. It is expected that the precision and accuracy of the determinations will be similar for the two fuels (see the preceding paper on processing Chalk River fuel).

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QUESTION AND ANSWER SESSION - SAVANNAH RIVER

F. Baranowski:

We have several questions directed to Harold Hull and John Langhaar regarding the Savannah River presentations.

"Does the exposed expansion tank cause you problems in freezing, or potential problems in possible loss of water in the shipping casks?"

Response - J. Langhaar:

The answer is yes, these exposed expansion tanks do cause problems. There are some disadvantages to having these external expansion tanks.

The disadvantages are, as indicated here, the problem of the freezing in cold weather, the vulnerability of the external piping to damage, and possible loss of water in the event that a cask should be overturned in a railroad accident, for example, and furthermore, this external hardware does increase and complicate the decontamination efforts required.

Now, we have used the external expansion tanks in casks where heat dissipation through the lid of the cask has appeared advisable or necessary. What we think is a preferred design in cases where this heat dissipation is not a problem, is an air space underneath the lid of the cask to accommodate the expansion. Then, after the cask is removed from the basin water, the cask water level would be lowered to a point perhaps a couple of inches below the under-surface of the lid to allow for expansion when the temperature rises. Of course the cask would be vented; in all cases it would be vented to the atmosphere.

Now, in order to take care of the freezing problem, in cases where we do have the external expansion tank, we have the piping so arranged that the water can enter the expansion tank from the cask, but cannot pour back from the expansion tank into the cask. In the

winter time we will use methanol as an anti-freeze in the expansion tank.

"Should not all PRDC fuel elements be shipped in sealed containers in case of failure en route to SRP?"

Response - J. Langhaar:

I think that we in the receiving and handling end of the business would like to see the elements all shipped in sealed containers, although it would introduce additional operations in the event that we had to remove the stainless steel housing. I am not sure how this would affect the dissolving operations.

Harold, can you answer this on the basis of our receiving all fuel elements in sealed aluminum containers with direct charging into a dissolver.

H. Hull:

The processing of additional aluminum amounts to extra steps, extra time, and extra waste. I wasn't sure, did this question apply to the PRDC?

J. Langhaar:

The PRDC only.

H. Hull

It would seem that putting each one in an aluminum can is apt to interfere with our method of criticality control. It might mean handling one core sub-assembly at a time instead of four.

H. Hull:

The next two questions are similar to each other.

"You indicated that four PRDC elements will be packaged in a flat array, four bundles, face-to-face. How do you avoid criticality problems?"

and

"Would you comment further on the problem of nuclear safety from processing PRDC cores?"

Response - H. Hull

Well, going a little further into it, a single PRDC core

sub-assembly of 144 pins, of the first type design has a neutron multiplication factor that is estimated to be about .65 in light water.

Four of them, placed side by side and fully submerged in light water, at the spacing dictated by the bird-cage result in a neutron multiplication factor of .88. A factor of 1 would be equivalent to borderline criticality.

Now, for this set-up, the uranium to hydrogen ratio is not at the optimum for fission, so that as the elements dissolve, the multiplication factor increases, so the specialists have made quite a number of calculations and have indicated that with four core sub-assemblies in a line, they go a little bit higher than .88, but, not enough higher to use up all of their safety factors.

With five core sub-assemblies, the approach is too close for comfort, and that has set the dissolver charge.

At this point, I might note that it is easily conceivable that future designs of core sub-assembly for this reactor might be more reactive, and it would seem that, in general, for fast reactors, the reactor designer might be able to employ a design that would make it extremely difficult to process the fuel and control criticality.

If design is such that a close approach to criticality is made for shipping a single sub-assembly in a cask full of light water, then criticality would be reached during dissolving when the reactivity goes up, as the uranium-hydrogen ratio changes.

Our primary control, as I visualize it, is the canyon shield. The fission products present with the irradiated fuel make this shield necessary, and the shield gives the personnel protection.

Various incidents in the past, and experiments and calculations by the appropriate specialists have indicated that the size of these incidents will be small enough for the shielding to protect the personnel.

One might look at it from the standpoint of reactor design, which is out of my field, but I would say it this way: these dissolver systems have a negative temperature co-efficient, and tend to be self-limiting, however, this still leaves us with a problem of possible damage to the equipment or spread of contamination through generation of gasses and pressure, and we don't intend to rely on the shield completely.

The next line of defense would be the control of concentration, which we will keep below the concentration for criticality in an infinite aqueous array, which runs approximately 12 to 13 grams of

U-235 per liter.

We set up the process to keep below this concentration, and we set up a number of safeguards to make sure that we don't get out of the process conditions. For example, in the dissolver itself, the fuel is kept at a high enough level in the dissolver so that the heat of reaction of the fuel with the liquid could not be used to boil off the water and allow the concentration to exceed safe limits.

The steam coils in the dissolver, that are used to bring the dissolver up to the boiling temperature, are located high in the dissolver, so that in an off-standard condition where the solution level had dropped below the bottom of the steam coils, we would still be below the critical concentration with 20 kilograms of U-235 in solution.

Going on down the process to the mixer-settlers, reflux of the U-235 is a possible means of concentration in the mixer-settler. The first thing that we do here is to insure that the process conditions will be such as to avoid reflux.

One case that results in reflux is leaving acid out of the scrub-stream. We will use samples and instrumentation (conductivity meters) to check on the acidity. We will use flow meters, back-up flow meters, to assure that the flows are such as to avoid reflux.

Further, it is possible to use two instruments for detecting reflux. One of these is a colorimeter, and in applying this instrument, we would pull a sample from a particular place in the mixer-settler that is apt to be a trouble spot. The sample will go up to the sample aisle continuously, and then go through a cell in the colorimeter and we will have a continuous monitor then, on the uranium concentration at that point.

The other instrument is a neutron monitor, and it is located down, or will be located down with the mixer-settler, and won't be subject to, say the possibility of sampler failure, like the colorimeter will. It consists, in part, of a neutron source; neutrons from the source pass through the solution, are possibly multiplied, and are detected by the neutron-counter.

So, in summary, we have a number of ways to assure that the concentration remains well below the danger point.

FUEL PROCESSING FACILITIES AT ORNL

H. E. Goeller*

This paper is a presentation of the general contribution which ORNL expects to make to the Commission's Interim Reactor Fuel Processing Program and includes a description of the fuels to be processed; an enumeration of the processes to be used; a discussion of the facilities, both existing and planned, in which processing will be done; a brief summary of our construction and operating schedules; and an enumeration of some of the major problems which confront us under the program. These topics will all be expanded in the four papers which follow.

1.0 DISCUSSION OF FUELS

1.1 Fuels Assigned to ORNL

Under the Commission's Interim Processing Program we have been assigned the responsibility for processing five domestic power reactor materials, namely, the fuel assemblies from the N. S. Savannah, Consolidated Edison, Rural Cooperative, and CPPD reactors and the blanket elements from the PRDC reactor. In addition, we have also been assigned responsibility for the Foreign Research Reactor fuels in the 20% U-235 enrichment range and fuel and blanket materials from aqueous homogeneous reactors. Finally, inasmuch as ORNL's program is primarily one of research and development of new processes through the pilot plant stage, we anticipate receiving a number of fuels from test reactors and possibly part cores from power reactors not directly assigned to us. Test reactor fuels which we expect to process include those from Borax-IV, SRE (Cores 1 and 2), EBWR, and possibly APPR.

1.2 Fuel Descriptions

The range of sizes, weights, and geometries represented by these fuels is presented in Fig. 1. In this illustration all elements are

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* Oak Ridge National Laboratory

Fig. 1—Relative sizes and weights of power reactor fuel assemblies.

to the same scale; the dotted lines indicate the parts, top and bottom, which would be removed prior to reprocessing and the darkened area the fuel-bearing section of the assembly. The ORNL Graphite Reactor slug and the MTR assembly illustrated at the left are typical of the size of fuel element on which the present reprocessing technology at ORNL is based. The weights of these fuels are in all cases no more than a few pounds. Thus it is apparent that a large extension in handling techniques, particularly with regard to weight, is involved in the handling of the power reactor fuels. Of the proposed fuels assigned to ORNL, the N. S. Savannah fuel has the largest cross section (8.7 sq in.), CPPD the greatest length (15 ft 4 in. with end sections removed), and Consolidated Edison the greatest mass (450 lb).

The complexity of the fuel assemblies is illustrated in Figs. 2-7. It should be noted that all these assemblies except the SRE and CPPD are based on a square array of tubes, varying from 16 tubes for the PRDC blanket element to 164 tubes in the N. S. Savannah assembly. The SRE and CPPD assembly tubes are arranged in a circular array of 7 and 19 tubes, respectively. Tubes are joined by four methods—ferrules in the Consolidated Edison fuel and sheet metal web spacers and end spiders in the CPPD; tube sheets are also used on other assemblies not illustrated such as Yankee Atomic. The model of the Commonwealth Edison assembly that is illustrated is only one-half full length; this fuel will be processed at Hanford.

1.3 Grouping of Fuels into Classes

In the discussions following, fuels are grouped into several classes for simplification. The first group, represented by Consolidated Edison and Rural Cooperative, are the stainless steel-clad $\text{ThO}_2\text{-UO}_2$ fuels. The second group contains the stainless steel-clad UO_2 fuels and is represented by the N. S. Savannah reactor fuel. The third group includes the stainless steel-clad NaK (or Na) bonded uranium or thorium metal or alloy fuels and is represented by the SRE (Cores 1 and 2) and CPPD fuels and the PRDC blanket. The fourth group is a miscellaneous group of varying types and includes the Foreign Research Reactor aluminum-clad 20% enriched uranium-aluminum alloy or U_3O_8 fuel; Borax-IV (aluminum-clad lead-bonded $\text{ThO}_2\text{-UO}_2$) fuel; uranyl sulfate solution, ThO_2 slurry, and possibly $\text{ThO}_2\text{-UO}_2$ slurry from the aqueous homogeneous reactor; the APPR fuel (stainless steel-clad, UO_2 —stainless steel cermet); and the EBWR Core 1 fuel (zirconium-clad uranium-zirconium-niobium alloy).

2.0 FUEL PROCESSES

All the above fuels will be readied for solvent extraction at ORNL by one of seven head-end processes, four of which are newly developed and three of which are based on well established technology. A schematic flowsheet of the several systems is given in Fig. 8.

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Fig. 2—Prototype fuel element, N. S. Savannah.

Fig. 3—Prototype fuel element, Commonwealth Edison.

Fig. 4—Model of Consolidated Edison fuel element ($\frac{1}{3}$ actual length)

Fig. 5—APDA axial assembly.

Fig. 6—SRE fuel element

Fig. 7—Consumers Public Power fuel cluster.

Fig. 8—Schematic ORNL over-all head-end flowsheet.

2.1 Head-End Processes

The three processes now used, in stainless steel equipment, are: (1) the Purex process for aluminum-clad uranium or UO_2 fuels in which the aluminum is first declad in sodium hydroxide and the uranium dissolved in nitric acid; alternatively, the cladding and uranium can be dissolved simultaneously in nitric acid and sodium nitrate; (2) the Thorex process for aluminum-clad thorium, thorium-uranium alloy, ThO_2 or $\text{ThO}_2\text{-UO}_2$ in which the fuel and clad are both dissolved in fluoride-catalyzed nitric acid; and (3) the MTR process for aluminum-clad uranium-aluminum alloy fuels in which the fuel is dissolved in mercuric nitrate-catalyzed nitric acid. The resulting dissolver solutions are processed further by concentration by evaporation or by dilution, and, in the case of fuels containing appreciable amounts of solids, by centrifugation (or possibly filtration).

The three new chemical head-end processes to be used are the Darex process which uses titanium equipment and the Sulfex and Zirflex processes which will use Nionel equipment. The Zirflex process can also be carried out in existing 309 SNb stainless steel equipment. The Darex process for all non-NaK-bonded stainless steel-containing fuels involves dissolution of non-thorium-containing fuels in dilute aqua regia, addition of concentrated nitric acid to the dissolver solution, distillation of the chloride from the dissolver product for recycle to subsequent dissolution, evaporation of excess nitric acid, and dilution with water to the correct solvent extraction concentrations. Inasmuch as $\text{ThO}_2\text{-UO}_2$ is insoluble in dilute aqua regia, the Darex procedure becomes a decladding method for stainless steel-clad $\text{ThO}_2\text{-UO}_2$ fuels. The cladding solution from which the chloride has been stripped can be either sent to waste or spiked with small amounts of fluoride and re-used as the $\text{ThO}_2\text{-UO}_2$ core dissolvent. The Sulfex process for non-NaK-bonded stainless steel-clad uranium and thorium oxide, metal, or alloy fuels (but not UO_2 --stainless steel cermets) involves dissolution of the cladding in sulfuric acid, the solution being discarded. The exposed core material is then dissolved by standard or modified Purex or Thorex head-end flowsheets. The Zirflex process for Zircaloy-2-clad uranium and thorium oxide, metal, or alloy fuels (except uranium-zirconium-niobium alloy) involves the decladding of the Zircaloy-2 in ammonium fluoride and subsequent dissolution of the core by a Purex or Thorex head-end flowsheet. The uranium-zirconium and uranium-zirconium-niobium core alloys, although soluble in nitric acid, cannot be dissolved in this reagent because of the explosive nature of the reaction of uranium-zirconium alloy with nitric acid. To compensate for this deficiency, several modified Zirflex flowsheets have been developed in which the core is dissolved in cladding solution by addition of nitric acid and aluminum; the presence of the fluoride from the decladding step eliminates the explosion hazard.

The last head-end approach that will be used at ORNL is mechanical processing. All the power reactor fuels except the stainless

steel--clad UO_2 --stainless steel cermet and Zircaloy-clad uranium-zirconium-niobium alloy fuels have cores that can be safely dissolved in nitric acid. Thus, if the cladding is removed or mechanically broken up, the exposed cores can be dissolved by conventional means. We expect to demonstrate two such methods: (1) decladding of NaK-bonded fuels for which Darex or Sulfex is unacceptable because of the NaK-acid reaction explosion hazard and (2) shearing and leaching of all stainless steel fuels, particularly those with oxide cores. It should be noted that our plans for mechanical processing are, at present, exclusively a research and development effort. Before they can be relegated to an interim processing status, we would have to make appropriate changes and additions to the facilities and equipment to assure interim processing reliability.

2.2 Solvent Extraction Processes

The various solutions prepared by above-discussed head-end operations are solvent-extracted in existing stainless steel equipment by one of the four methods shown in Fig. 9. In the cases where large amounts of aluminum, zirconium, molybdenum, or stainless steel are present in the solvent extraction feed, the flowsheets will have to be modified in process details to accommodate these diluents. However, since the diluents report to the first cycle waste, only the first cycle operations are affected.

The Purex flowsheet as used at ORNL for low-enriched uranium-plutonium fuel solutions involves two cycles of co-decontamination. The uranium-plutonium stream is partitioned in a third cycle, and the uranium product is evaporated to 1-1.5 M $\text{UO}_2(\text{NO}_3)_2$ prior to shipment. The plutonium product is further processed by anion exchange to give a solution containing ~ 50 g of plutonium per liter and shipped. The Purex flowsheet uses 30% TBP and in its standard form uses 3 M HNO_3 salting.

The TBP-25 process for decontamination of U-235 is based on two cycles of solvent extraction with 2-6% TBP, depending on the ratio of diluent to uranium in the fuel. Salting is usually achieved solely by the aluminum or stainless steel diluent. The decontaminated uranium product is evaporated to approximately 1 M $\text{UO}_2(\text{NO}_3)_2$ for shipment.

Thorium-uranium fuels are solvent-extracted by either the Interim-23 or the Thorex process. The former uses approximately 6% TBP and has a first cycle thorium-uranium partitioning with the thorium reporting to the waste. The uranium is solvent-extracted in one or more additional cycles with 6% TBP. The uranium is finally processed by evaporation or cation exchange for final cleanup and concentration. The Thorex process involves co-decontamination of the uranium and thorium with 42% TBP. When Amsco is used as the solvent diluent, an acid-deficient or low-acid flowsheet is required. However, it has recently been found possible to operate with a high-acid feed if

Fig. 9—Schematic ORNL over-all solvent extraction flowsheet.

42% TBP in Decalin or 30% TBP in Amsco is used as the solvent. The first cycle thorium-uranium product is then partitioned according to the Interim-23 second cycle.

The main advantage of a purely Interim-23 first cycle is its greater throughput; its chief disadvantage is the production of a high-activity level thorium-containing waste stream which cannot be further concentrated and must be stored in water-cooled waste storage tanks. The Thorex process produces a thorium waste that can be stored in conventional uncooled concrete tanks.

Since the decay activity from the Th-228 associated with the product thorium and the U-232 associated with the U-233 or mixed U-233—U-235 product will be high, we have assumed that both products from uranium-thorium processing will find no market in the near future and that they will both have to be stored indefinitely at ORNL as the nitrate solutions.

2.3 Processes to Be Used on Assigned Fuels

Fuel composition and burnup data and the planned method of processing of the various fuels assigned to ORNL are shown in Tables 1 and 2. Table 1 presents the data for fuels of classes 1, 2, and 3 and Table 2 for the miscellaneous fuels of class 4.

The stainless steel-clad low-enriched UO_2 class 2 fuels with burnups up to 10,000 Mwd/t will contain up to 5000 g (0.5%) of plutonium per ton and will be processed by Sulfex or Darex processes with some fuel reserved for shearing and nitric acid leaching development tests. Solvent extraction will be by the Purex process. The stainless steel-clad ThO_2 - UO_2 class 1 fuels will be irradiated up to 23,000 Mwd/t av. and will contain approximately 6% U-233—U-235 mixture after irradiation. This type of fuel will also be readied for solvent extraction by Sulfex or Darex head-end treatments and solvent-extracted by the acid-Thorex and/or acid—Interim-23 processes. Some of the class 1 fuels will also be reserved for mechanical processing development.

As already discussed, we have precluded the use of either Darex or Sulfex on the stainless steel-clad NaK-bonded class 3 fuels on the basis of safety. We therefore plan to declad these fuels, which will be burned up to 3000 Mwd/t av. and will contain up to 2000 g of plutonium per ton, by mechanical methods in order that the NaK may be reacted with steam prior to chemical processing. Subsequent to mechanical processing, the fuel will be handled, both in head-end and solvent extraction operations, by standard or modified Purex or Thorex processes. The undissolved stainless steel will be compacted and handled as a solid waste material.

In dissolution of declad NaK-freed SRE fuels, we envision no chemical problems, since Core 1 fuel is unalloyed uranium and Core 2 is a

Table 1. Fuel Data and Proposed Process for Classes 1, 2, and 3 Fuels

<u>Fuel Type</u>	<u>Fuel</u>	<u>Mwd/t av.</u>	<u>Core Composition</u>	<u>U Enrichment</u>	<u>Proposed Process</u>
Stainless steel —clad UO ₂	N. S. Savannah	7,400	UO ₂	4.2 and 4.6%	Sulfex-Purex or Darex-Purex
Stainless steel —clad ThO ₂ -UO ₂	Consolidated Edison	23,000	[5.5% UO ₂ , 94.5% ThO ₂ 7.2% UO ₂ , 92.3% ThO ₂ 8.6% UO ₂ , 91.4% ThO ₂	[Full Full Full	Sulfex-Thorex or Interim-23 Darex-Thorex or Interim-23
	Rural Cooperative	5,500	4.5% UO ₂ , 95.5% ThO ₂	Full	
Stainless steel —clad NaK- bonded alloy	SRE Core 1	~ 1,000	U	2.80%	Mechanical Decladding and Purex
	SRE Core 2	?	7.6% U, 92.4% Th	Full	
	PRDC Axial blanket	≤ 1,000	97.5% U, 2.5% Mo	Depleted	
	PRDC Radial blanket	2,500*	97.5% U, 2.5% Mo	Depleted	
	CPPD Core 1	3,000	90% U, 10% Mo	3.55%	

* Maximum

Table 2. Fuel Data and Proposed Processes for Miscellaneous Fuels

<u>Fuel</u>	<u>Clad</u>	<u>Bond</u>	<u>Core Composition</u>	<u>U Enrichment</u>	<u>Proposed Process</u>
Foreign Research Reactors (20% U-235)	Al		U-Al alloy or U ₃ O ₈	20%	HNO ₃ [Hg(NO ₃) ₂] —TBP-25
Homogeneous			UO ₂ SO ₄ solution	Full	Dilution—TBP-25
			ThO ₂ or ThO ₂ -UO ₂	Full	Thorex
Borax-IV	Al	Pb	ThO ₂ -UO ₂	Full	NaOH, dilute HNO ₃ , Thorex
APPR Northern States Superheater	} Stain- less steel		UO ₂ --stainless steel cermet	Full	Darex—TBP-25
EBWR Core 1					
	Zr		U, 5% Zr, 1.5% Nb	Natural and 1.44%	Modified Zirflex or Zircex

thorium-uranium alloy, both of which can be handled readily by existing technology. With the PRDC blanket and CPPD Core 1 fuel, some, though not serious, problems are anticipated because of the molybdenum alloyed with the uranium in the fuel. The major problem appears to be selection of a process that will give a minimum volume of high-activity aqueous waste.

Table 2 summarizes the fuel and proposed processing data for the miscellaneous fuels. The Foreign Research Reactor, Homogeneous Reactor, and Borax-IV fuels are all representative of fuels for which the reprocessing technology is well developed and may be applied with only minor modifications. The only problem anticipated in processing the Foreign Research Reactor and MTR type fuels is the solution-solids separation which results from the high silicon content in the fuel and for which we plan to use centrifugation. The lead bond in the Borax-IV fuel is a new type of bonding agent which presents a fuel dissolution problem. However, a satisfactory three-step flowsheet has been demonstrated on unirradiated fuel samples in which the aluminum cladding is dissolved first in caustic, the lead bond in dilute nitric acid, and finally the $\text{ThO}_2\text{-UO}_2$ in fluoride-catalyzed nitric acid. In a two-region aqueous homogeneous thorium breeder, the fuel is a fully enriched uranyl sulfate solution in D_2O and the blanket is a thorium oxide slurry in D_2O . Both are easily processed by a standard Thorex method. The Thorex feed is prepared, after D_2O removal, from the uranyl sulfate solution by adding dilute nitric acid and from the ThO_2 slurry by dissolution in fluoride-catalyzed nitric acid. In a single-region thorium breeder, the fuel is a $\text{ThO}_2\text{-UO}_2$ slurry in D_2O , which is processed by the same method as the blanket of a two-region reactor. The only difference is that more stringent criticality control is required in reprocessing the single-region fuel.

The remaining two fuels, from the APPR and EBWR Core 1, are representative of the two currently-used fuel types which are not amenable to either chemical or mechanical decladding methods. The APPR fuel, which is a multiplate fuel with stainless steel cladding and fully enriched UO_2 -stainless steel cermet core, is readily solubilized by the Darex process. The enriched uranium is then recovered by a modified TBP-25 solvent extraction process. The EBWR Core 1 fuel also is a multiplate assembly; however, the core material is in the form of low-enriched uranium-zirconium-niobium alloy clad in Zircaloy-2. It is proposed to reprocess this fuel by a modified Zirflex head-end process and a modified Purex solvent extraction process.

3.0 DESCRIPTION OF ORNL FUEL REPROCESSING FACILITIES

The facilities at ORNL for reprocessing irradiated reactor fuels are of four functional types: (1) head-end facilities for the receipt, storage, dissolution, and feed adjustment of the various fuels; (2) solvent extraction equipment for separation and decontamination of the fissionable, fertile, and inert materials in the fuel and isolation of

the various fertile and fissile products; (3) by-product handling facilities for the purification and packaging of fission product and trans-uranic elements; and (4) radioactive waste handling and/or storage facilities for the radioactive off-gas, aqueous wastes, and solid wastes generated in the foregoing three areas.

3.1 Fuel Receipt and Decay

Figure 10 shows schematically the methods by which fuel shipments from the reactor operators will be handled from the time of receipt to the dissolver loading operations. The fuel can be delivered to Oak Ridge in shielded casks by motor transport, rail, or barge. The casks will be monitored for surface activity and temperature at the receiving point. Motor transport cask deliveries will be made directly to the ORNL Bldg. 2527 canal area; weight restrictions (up to 75 tons) are subject only to arrangements made between the reactor operator and the various state highway departments. Rail shipments will be limited to a maximum loaded cask weight of 75 tons and will be made to the Blair, Tennessee, station of the Southern Railway Company, from where the railway car will be moved by yard engine to K-25. Barge shipments will be made to the K-25 dock on the Clinch River and will be limited to 28 tons. Rail- and barge-shipped casks will be transferred at K-25 to a 100-ton lowboy for motor transshipment to ORNL. Rail shipments up to 60 tons will be transferred to the lowboy at the K-25 power house (K-1501) by use of a 60-ton building crane; casks from 60 to 75 tons will be transferred at the K-25 rail head by two 60-ton mobile cranes. Barge shipments will be transferred at the K-25 dock to the 100-ton lowboy by the existing 28-ton jib crane.

On receipt of the cask at the Bldg. 2527 canal, samples of the coolant, and of the gas in the space above, will be taken to determine conformance with cask acceptance criteria. If conformance is assured, the cask will be transferred from the lowboy to the bottom of the 35-ft-deep cask unloading basin with the 75-ton Bldg. 2527 bridge crane and the cask cover loosened by long-handled impact wrenches and removed by the 10-ton auxiliary on the building bridge crane. The canned or uncanned fuel assemblies will be removed individually with the 1-ton electric hoist on either of the two canal traveling work bridges and transported vertically to the fuel storage basin, where they will be stored in critically safe arrays pending reprocessing.

When the fuel is ready to be reprocessed, the assemblies will be transported to the underwater saw, where the inert end sections of the assembly will be removed unless already removed by the reactor operator. The inert ends will be collected and ultimately delivered to the burial ground in a special disposal cask. The active section of the assembly will then be loaded into a fuel charger for charging to one of the several head-end processing facilities at ORNL.

The three isotopes which in large degree govern the fuel decay

Fig. 10—Fuel handling operations prior to dissolution or mechanical processing.

time prior to reprocessing are U-237 and I-131 for uranium and Pa-233 and I-131 for thorium. In both cases the 8-day I-131 activity is an extreme health hazard which is released as a gaseous product during dissolution and which must be eliminated by long decay or effective removal from the off-gas stream. About 8.6×10^{-2} curie/day can be discharged safely from the Bldg. 3019 stack. The tolerance in air of I-131 is 1.8×10^{-8} $\mu\text{c/cc}$. The new off-gas filters and silver-coated copper-mesh iodine adsorption units located at the 3039 stack are expected to remove all but 0.01% of the iodine released in reprocessing.

The U-237 specification for product uranium specifies that the beta and gamma activity from the U-237 in the product shall not exceed that of natural uranium in equilibrium with the beta and gamma activities of its daughters. Studies made to date indicate that the U-237 is generally controlling if all but 0.01% of the iodine can be effectively removed. For example, in the case of PRDC blanket material irradiated to a maximum of 6000 Mwd/t, 100 days' decay is required for U-237 decay but only 80 days for I-131.

In the case of thorium fuels, the 27.4-day Pa-233 activity is controlling, particularly if time is allowed to permit quantitative decay to U-233, which requires 6-8 months' decay. We plan to permit decay to > 99.9% U-233.

3.2 Reprocessing Facilities at ORNL

Figure 11 is a schematic plot plan of the ORNL facilities as they will exist about January 1962, after completion of the plant reprocessing additions now in design. The fuel reprocessing head-end and solvent-extraction facilities are housed in Bldgs. 2527, 3019, and 3505, and the by-product handling facilities are in Bldgs. 3517 (fission products) and 3508 (transuranics). Aqueous waste facilities include the high-activity storage tanks just east of Bldg. 2527, the intermediate activity tanks north of Bldg. 3505, and the low-activity waste lime-soda treatment plant and settling basins south of Bldg. 3517. Off-gases are discharged to three stacks, the Bldg. 2527 stack, the 3020 stack, and the main plant stack 3039. Solid wastes are transported to the burial ground about 1 mile west of Bldg. 2527. The experimental mechanical processing facilities are in Bldg. 3026.

As previously described, fuel casks are delivered to the Bldg. 2527 canal and placed in the cask unloading pit which is 20 x 15 x 35 ft deep. After removal from the cask, the fuel assemblies are stored in one of the two fuel storage canals, which provide a total storage area of 1800 sq ft x 24 ft deep. When ready for processing, the assemblies are moved to the fuel charger loading area and placed in a charger for delivery to one of the several dissolver systems. The over-all dimensions of the canal facilities are about 32 x 100 ft. Auxiliaries to the canal area include a cask decontamination pad, where the empty cask is cleaned up prior to return to the reactor

Fig. 11 — Processing facilities at ORNL. (For meanings of letters and numbers, see list on next page.)

Meanings of Letters and Numbers
on Fig. 11, Processing Facilities at ORNL

2527	New Head-End Facility	A	Fuel Cask Unloading Pit	O	Operating Area
3019	High-Activity Head-End and Solvent Extraction Facility	B	Fuel Storage Canals	P	Sampling Area
		C	Fuel Charger Loading Station	Q	Plant Administrative Area
3020	Bldg. 3019 Cell Off-Gas Stack	D	Fuel Cask Decontamination Pad	R	Cold Analytical Laboratory
		E	Canal Demineralizer Pit	S	Hot Analytical Laboratory
3026	Mechanical Processing Facility	F	Darex Head-End Cell		
		G	Sulfex Head-End Cell	U	Off-Gas I ₂ Removal System
3039	Main Plant Stack	H	Darex-Sulfex Operations Area	V1	High-Activity Aqueous Waste Storage
3505	Intermediate-Activity Head-End and Solvent Extraction Facility	I	Darex-Sulfex Sampling Area	V2	Intermediate-Activity Aqueous Waste Storage
		K	Rare Gas Removal System	W	Conventional Head-End Facility
3508	Transuranic Element Processing Facility (dotted lines indicate proposed addition for Cf handling)	L	Cell Off-Gas Filter Equipment	X	Pu Isolation and Loading Area
		M	Interplant Piping Tie-Lines	Y	Fuel Decladding and Chopping Cell
		N	Existing High-Level Processing Cells	Z	Fuel Leaching Cell
3517	Multicurie Fission Product Pilot Plant	1 & 2	Volatility Process Pilot Plant	AA	Scrap Handling Cell
		3	U-233 Rework Equipment		
		4	U-Pu Rework System		
		5	Conventional Head-End System		
		6 & 7	First and Second Cycle Solvent Extraction		

operator, and a 175-gpm canal water demineralization system. Small fuel storage canals currently exist at Bldg. 3019 and Bldg. 3505 but are of limited use because they are only 10 ft deep and have only 10-ton-capacity hoisting facilities.

The remainder of Bldg. 2527, which is 65 x 75 ft, houses the Darex and Sulfex-Zirflex head-end systems. Cells F and G are each 20 x 25 x 30 ft deep and have 6 ft of concrete shielding and full-opening roof slabs. The area above the cells is also served by the 75-ton canal crane. The south cell (F) contains the Darex and Sulfex-Zirflex dissolvers, the common head-end centrifuge, and auxiliaries; the north cell (G) houses the Darex chloride-removal system and common final feed adjustment equipment. The area west of the cells is a three-floor nonradioactive area, 30 x 65 ft. The top floor is the head-end makeup, operating, and control area; the middle level, the administrative and change room area; and the basement, the building general services and utilities area. The area east of the cells is 12 x 65 ft. The top level contains the process solution sampling facilities and instrument transmitters, and the basement a series of vulnerable equipment pits; the middle area is open and is reserved for pit servicing. Controlled access to the operating area, the cell roof, the east area, and the canal is via the change area. The area north of the cell will be kept clear for future cell expansion.

Solvent-extraction feed solutions prepared in Bldg. 2527 are pumped to Bldg. 3019 via the underground interplant tie-line system which interconnects the various building process and waste systems in the complex.

Building 3019, which is about 80 x 300 ft, contains a set of seven processing cells 20 x 20 x 27 ft deep with 5-ft concrete-shielded walls. The operating area and sampling area are arranged in a manner similar to the corresponding areas in Bldg. 2527. Cells 1 and 2 house the ORNL Fluoride Volatility Pilot Plant and cells 3-7, the Bldg. 3019 Power Reactor Fuel Reprocessing facilities, including the high-activity level conventional fuel head-end system (cell 5), two cycles of solvent extraction (cells 6 and 7), and rework system (cell 4), and a low-capacity U-233 solvent-extraction rework system (cell 3). The general administrative area for the entire complex is housed in Bldg. 3019.

Analytical facilities for the reprocessing program are housed in Bldg. 3019 and include a nonradioactive analytical and counting laboratory and an eight-cell radioactive analytical laboratory. Uranium-233 and U-235 ion exchange isolation facilities are also located in the nonradioactive analytical area. The tank pit south of Bldg. 3019 contains three tanks with a total volume of 25,000 gal for storage of intermediate-activity thorium product.

Building 3505, which is 60 x 80 ft, has one cell 18 x 20 x 20 ft

deep, one cell 8 x 8 x 20 ft deep, both with 2 ft of concrete shielding, and five cells 8 x 8 x 20 ft deep with 8 in. of concrete shielding. In addition, an intermediate-activity-level conventional fuel dissolver facility is located in a pit between the Bldg. 3505 canal and the first cell. The large cell contains solvent extraction feed and waste collection tankage and the first 8 x 8 ft cell the uranium-plutonium partitioning cycle extraction column. The remainder of the partitioning cycle, the fourth uranium cycle (which will not be used), and the plutonium anion exchange final cleanup and concentration equipment are located in the five 8-in.-concrete shielded cells. The plutonium storage vault, located east of Bldg. 3508, will be used to store plutonium product solutions pending shipment.

The mechanical processing facility which will be housed in Bldg. 3026 will be used for research and development demonstrations of various techniques on a variety of fuels. Two cells with manipulators, windows, and 5 ft of concrete shielding are available. The south cell, which is 10 x 25 x 15 ft deep, will be used for fuel decladding and shearing studies; the north cell, which is 10 x 15 x 15 ft deep, will be used for fuel leaching studies. Part of the interplant tie-line system from Bldg. 3026 to Bldg. 3019 will permit transfer of leach solutions for subsequent feed adjustment and solvent extraction at the latter facility. A small storage cell will be used for the storage of declad fuel that has been recanned and scrap pending final disposition to Bldg. 3019 and the burial ground, respectively.

As already mentioned, the off-gases are of three types: from the cells, from the process vessels, and from the dissolvers. The cell off-gas from Bldg. 2527 passes through an underground duct to the filter pit, which houses two parallel sets of triple filters, each including a roughing filter and two CWS type finishing filters in series. This off-gas stream is then routed through a blower and up the 100-ft Bldg. 2527 steel stack. The system has a capacity of 13,000 cfm and maintains 0.2-0.3 in. H₂O vacuum in the cells.

Vessel off-gas from Bldg. 2527 is routed via an underground 8-in. stainless steel line to the 250-ft 3039 stack. The decladding and dissolver off-gases from Bldg. 2527 operations are first scrubbed with caustic solution and then processed through a low-temperature distillation rare gas removal system. The krypton-free dissolver off-gas is then combined with the vessel off-gas. Hydrogen-containing dissolver off-gases may be burned by submerged combustion prior to being combined with the vessel off-gas sent to the 3039 stack.

The cell off-gas from Bldg. 3019 will be filtered and then discharged up the 200-ft 3020 stack. Dissolver off-gas generated in Bldg. 3019 equipment will be scrubbed with caustic, combined with the vessel off-gas, and sent to the 3039 stack via a 10-in. stainless steel line. The cell off-gas from Bldgs. 3505 and 3517 will be combined and routed through a 54-in. concrete pipe to the 3039 stack. The dissolver and

vessel off-gases from Bldg. 3505 will be discharged through a stainless steel line also to the 3039 stack.

The highest-activity aqueous wastes will emanate from the first cycle solvent extraction system in Bldg. 3019 and will be routed via the interplant tie-lines to the water-cooled stainless steel waste storage tanks. The three tanks will be housed in a 5.5-ft concrete-shielded pit 35 x 45 ft. Each of the three tanks will have 15,000 gal capacity and sufficient heat removal capacity for the removal of 2,500,000 Btu/hr from the waste solution stored at a maximum temperature of 160°F.

Head-end decladding waste from Bldg. 2527 and solvent extraction wastes, other than from the first cycle, from Bldgs. 3019 and 3505 will be sent to the six 170,000-gal concrete waste tanks. Low-activity process and service wastes, after proper monitoring, will be discharged via the lime treatment plant to the settling basins located south of Bldg. 3517. The basins discharge via White Oak Creek and Lake to the Clinch River.

Solid wastes from end box removal in the Bldg. 2527 canal and from mechanical processing in Bldg. 3026 will be delivered in shielded carriers to the ORNL burial ground located about 1 mile west of the ORNL area.

Building 3517, the Multicurie Fission Product Pilot Plant, will be used to process Bldg. 3019 first cycle solvent extraction wastes to recover up to 100,000 curies of marketable fission products such as cesium and strontium. In Bldg. 3508 similar wastes will be processed for recovery of transuranic elements such as americium and curium, which will be used primarily for research and development purposes. The present facilities are adequate for isolation of milligram quantities of curium. The addition shown by dotted lines will permit isolation of gram quantities of curium and 0.1 g quantities of californium. The interplant tie-line system permits delivery of the solvent extraction wastes to these two facilities by pipe line.

3.3 Capacity of ORNL Facilities

In almost all cases, the capacity of the ORNL fuel reprocessing facilities is limited by the existing Bldg. 3019 solvent extraction equipment. Figure 12 shows schematically the existing columns at Bldgs. 3019 and 3505, the flow pattern for the various types of feeds, and the nominal capacities for the several products. In all cases the capacities given are nominal values, which we feel can be maintained for relatively long periods of operation; considerably higher throughputs for both uranium and thorium have been observed for short operating periods.

Based on Bldg. 3019 operations, the low-enriched uranium capacity

Fig. 12—Solvent extraction facilities and capacities at ORNL.

(up to ~ 5% U-235 enrichment) for standard Purex processing is 300 kg/day. The corresponding thorium capacity is 300 kg/day for the Acid Interim-23 flowsheet, in which thorium is sent to waste, or 200 kg/day for the Acid Thorex flowsheet, in which there is a one-cycle decontamination of the thorium. The plutonium capacity is limited by capacity of the plutonium isolation system in Bldg. 3505, which is 3-5 kg/day of plutonium. The capacity of the Bldg. 3019 facilities for fully enriched U-235 is 5-10 kg/day. The capacity for U-233 and U-233--U-235 mixtures is about 15 kg/day for the first two cycles. The capacity of the smaller U-233 rework system (third uranium cycle) is about 2 kg/day.

All capacities enumerated above are for fuel solutions containing only small amounts of aluminum, stainless steel, or zirconium diluents. For fuel solutions containing large amounts of such diluents, the capacities will be correspondingly reduced; for example, the stainless steel/uranium ratio in the APPR fuel decreases the capacity to ~ 5 kg/day of uranium and the aluminum/uranium ratio in the Foreign Research Reactor fuels decreases the capacity to ~ 25 kg/day of uranium (or 5 kg/day of U-235).

4.0 CONSTRUCTION AND OPERATING SCHEDULES

Our tentative construction and fuel reprocessing schedule for the Power Reactor Fuel Reprocessing program is shown in Table 3. All construction and modifications of present facilities are scheduled to be completed by January 1962; however, certain facilities will be operable considerably earlier, such as the Bldg. 2527 canal, which will be completed in January 1961, and the modifications to the present solvent extraction and plutonium isolation systems, which are scheduled for March 1961. The Darex-Sulfex head-end facility will be completed in January 1962 and is expected to be ready for processing of irradiated fuel by April 1962 after 3-4 months of equipment cleanup and calibration and nonradioactive runs on stainless steel and Zircaloy scrap and possibly low-radiation runs on rejected fuel material.

Fuels that we plan to reprocess in existing facilities prior to the completion of Bldg. 2527 construction include the SRE Core 1 and Borax-IV in 1960 and the SRE Core 2 and the first of the Foreign Research Reactor 20% enriched U-235 cores in 1961. Of the fuels assigned to ORNL that will be reprocessed in Bldg. 2527, the first PRDC blanket material and the EBWR Core 1 will be reprocessed in 1962, the first N. S. Savannah, Rural Cooperative, and Consolidated Edison cores in 1963, and the first CPPD fuel in 1964.

Table 3. Construction and Reprocessing Schedule
for ORNL PRFR Facilities

Construction Schedule

Canal and head-end building (2527)	January 1961
Changes to solvent extraction and plutonium isolation systems	March 1961
Installation of Darex-Sulfex systems	January 1962
Completion of Darex-Sulfex shakedown and start of radioactive operations	April 1962
SRE decladding (research and development only)	January 1960
Shearing and leaching	October 1961

Reprocessing Schedule

SRE Core 1	April 1960
Borax-IV	May 1960
First Foreign Research Reactor (20% U-235)	May 1961
SRE Core 2	June 1961
PRDC blanket	May 1962
EBWR Core 1	December 1962
N. S. Savannah	January 1963
Rural Cooperative	August 1963
Consolidated Edison	Sept.-Oct. 1963
CFPD	February 1964

CHEMICAL PROCESSING OF POWER AND RESEARCH REACTOR FUELS
AT OAK RIDGE NATIONAL LABORATORY

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1.0 INTRODUCTION

The chemical processes presented in the following sections represent those selected for use in the Oak Ridge National Laboratory Power Reactor Fuel Reprocessing Pilot Plant as of October 1959. Many of the processes will be changed considerably as development work proceeds. The completeness of development work varies. For example, the development of the Darex and Sulfex processes is in an advanced stage, whereas those for molybdenum-bearing fuels and Acid Thorex extraction are in a preliminary stage. An absolute choice of processing conditions is not required at present since the equipment is designed to test the relative efficiency of alternative flowsheets and thus meet the objectives of a pilot plant. The processes selected do not necessarily represent the best over-all approach for a new plant since many decisions were made to make the best possible use of existing processing and waste storage facilities.

Many processes now being developed at ORNL for fuel reprocessing are not described since they are not scheduled for early demonstration in the Pilot Plant. The Fluoride Volatility¹ and Zircex² processes for processing zirconium-bearing fuels are outstanding examples of processes under development. The Fluoride Volatility process is being demonstrated on a moderate size but full radiation level scale in a separate pilot plant at ORNL. Other important development work is directed toward methods for processing ceramic fuels, with initial emphasis on those containing graphite³ or beryllium.

Problems not presented in this report include corrosion, feed clarification, off-gas handling, and recovery of fragments of source and fissionable material from dissolver solutions. These items are reported in a separate paper.⁴

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2.0 CLASSIFICATION OF FUELS

The reactor fuels have been divided into classes based on processing criteria (Table 1). In the following sections, a single representative flowsheet and supporting development work are presented for each fuel class, where possible. For example, a flowsheet is shown for Consolidated Edison in the class I fuels since it can be applied with few modifications to Rural Co-operative or similar fuels. However, separate flowsheets and supporting data are given for the fuels in class III, i.e., fuels with sodium bonds, because of the great differences in core compositions.

Alternative processes, Darex and Sulfex, are listed in Table 1 for dissolution of class I and II fuels since it is an important objective of the pilot plant to determine the relative merits of these two processes. Similarly, two processes are listed for dissolution of the uranium-molybdenum fuels in class III, i.e., nitric acid or nitric acid-ferric nitrate dissolution. The former offers minimum high level radioactive waste volumes but poses a difficult operating problem in the removal of solid molybdic acid crystals from the dissolver solution. Conversely, the latter offers complete dissolution and hence minimized operating problems but large volumes of highly radioactive waste.

The designation of wastes as high or intermediate radioactive level wastes in Table 1 is based on the unique characteristics of the ORNL waste system. The 170,000-gal concrete waste tanks at ORNL can dissipate approximately 50,000 Btu/hr, and consequently the waste solutions must not exceed 18 curies/gal assuming an average 0.7 Mev/disintegration. Hence wastes containing less than 18 curies/gal are listed as "intermediate level." These wastes will be neutralized prior to disposal to the concrete tanks. Higher level wastes will be stored as acidic solutions in cooled stainless steel tanks (Sect. 5.0).

3.0 DISSOLUTION PROCESSES

3.1 Class I: Stainless Steel--clad Thorium Oxide-Uranium Oxide Fuels

The principal representatives of class I fuels, Consolidated Edison and Rural Co-operative, contain solid solutions of ThO_2 and UO_2 as cores enclosed in stainless steel tubes. Two alternative decladding processes have been developed for these fuels. The stainless steel may be dissolved in either dilute aqua regia (Darex process⁵) or sulfuric acid (Sulfex process⁶). Cores of either ThO_2 - UO_2 or uranium-thorium alloy are best dissolved in the Thorex⁷ dissolvent, 13 M HNO_3 --0.04 M NaF. Both processes will be evaluated in pilot plant operations. The following discussions use the Consolidated Edison fuel to illustrate the flowsheets and chemical variables. These data should be applicable to other fuels of this class with minor changes. The development work on class I fuels reported in the following sections was performed largely on unirradiated fuel samples. Data are now being obtained on irradiated samples.

Table 1. Chemical Processes for Fuels by Classes

Reactor	Dissolution Process	Extraction Process	Activity Level of Waste
<u>Class I Fuel: Stainless Steel--clad ThO₂-UO₂ Core</u>			
Consolidated Edison	Darex decladding		Intermediate
Rural Co-operative	HNO ₃ dissolution	Acid Thorex	High
	or		
	Darex dissolution	Darex-Thorex	High
	or		
	Sulfex decladding and		Intermediate
	HNO ₃ dissolution	Acid Thorex	High
<u>Class II Fuel: Stainless Steel--Clad UO₂ Core</u>			
Nuclear Ship	Darex dissolution	Darex-Purex	High
	or		
	Sulfex decladding		Intermediate
	HNO ₃ dissolution	Purex	High
<u>Class III Fuel: Stainless Steel--clad Sodium-bonded Cores*</u>			
SRE-I (U metal core)	Caustic decladding*		Intermediate
	HNO ₃ dissolution	Purex	Intermediate
SRE-II (Th-7.5% U alloy core)	Caustic decladding*		Intermediate
	HNO ₃ -F dissolution	Acid Thorex	Intermediate
CPPD-I (U-10% Mo core)	Caustic decladding*		Intermediate
	HNO ₃ dissolution	Purex	High
PRDC-Blanket (U-3% Mo core)	Caustic decladding*		Intermediate
	HNO ₃ -Fe dissolution	Purex	Intermediate
CPPD-II (UC core)	Caustic or steam decladding*		Intermediate
	HNO ₃ dissolution	Purex	High
<u>Class IV Fuel: Aluminum-clad Enriched U-Al Alloy Core</u>			
Foreign Research (20% enriched U-Al alloy core)	HNO ₃ -Hg dissolution	TBP-25	Intermediate
<u>Class V Fuel: Aluminum-clad Thorium in Core</u>			
Borax-IV (Al-clad Pb bond, UO ₂ -ThO ₂ core)	Caustic decladding		Intermediate
	Dilute HNO ₃ bond dissolution		Intermediate
	HNO ₃ -F dissolution	Acid Thorex	Intermediate
<u>Class VI Fuel: Zircaloy-clad Zirconium-Uranium Alloy</u>			
EBWR-I (5% Zr-1.5% Nb 93.5% U core)	Modified Zirflex	Purex	Intermediate
	NH ₄ F dissolution		
<u>Class VII Fuel: Aqueous Solution or Slurry</u>			
Homogeneous Reactor			
UO ₂ SO ₄ solution			
in D ₂ O	HNO ₃ dilution	TBP-25	Intermediate
ThO ₂ slurry in D ₂ O	HNO ₃ -F dissolution	Acid Thorex	Intermediate

*Stainless clad removed mechanically and replaced with aluminum can.

3.1.1 Dissolution of Consolidated Edison Fuel by the Darex-Thorex Process. The Consolidated Edison reactor fuel is typical of fuels in class I, being composed of a core of high-density 95% $\text{ThO}_2\text{-UO}_2$ pellets clad in 304 stainless steel. Decladding in boiling 5 M HNO_3 --2 M HCl (Fig. 1) requires 3 hr, yielding an undiluted waste solution containing about 50 g of stainless steel per liter and, with pellets that are 94% of theoretical density, less than 0.05% of the uranium.

Dissolution of the high-density core pellets in a 200% stoichiometric excess of boiling 13 M HNO_3 --0.04 NaF--0.1 M $\text{Al}(\text{NO}_3)_3$ will probably require about 20 hr. Aluminum is required in the dissolvent to suppress fluoride corrosion of the expected dissolver material, titanium.

In actual plant operation, both decladding and core dissolution will be semicontinuous. This should not markedly affect the decladding time but may lengthen the time required for core dissolution.

The main advantages of the Darex decladding process are: (1) dissolution of stainless steel is rapid and complete; (2) no hydrogen is evolved; (3) cross-contamination of solutions is not a serious problem; (4) uranium can easily be recovered from the decladding solution in the existing extraction system if losses are high; and (5) the decladding solution can be combined with concentrated nitric acid and used as the core dissolvent, thereby avoiding uranium losses (Fig. 2). The major disadvantage is the generation of relatively large volumes of highly radioactive waste if the decladding solution contains too much uranium to be discarded and is adjusted for use in core dissolution.

Dissolution rates of stainless steel in boiling 4 and 6 M HNO_3 reach maxima of 50 and 75 mg/min·sq cm when the hydrochloric acid concentration is about 2 M (Fig. 3).⁸ With hydrochloric acid concentrations between 2 and 4 M, the rates decrease to the nearly constant value of about 35 mg/min·sq cm obtained with hydrochloric acid concentrations greater than 4 M. This fact is particularly significant since, in some isolated cases, stainless steel in contact with a second metal is passive to boiling 5 M HNO_3 --2 M HCl . Since passivation basically is a transient phenomenon, the time required for initiation of the desired reaction is the variable of major concern. With stainless steel specimens that had been passivated in refluxing 15 M HNO_3 --0.3 M CrO_3 and in contact with titanium, the time required for depassivation in 5 and 6 M HNO_3 decreased from 2 to nearly 0 hr by increasing the hydrochloric acid concentration from 1 to 6 M (Fig. 4). If passivation is encountered in plant operation, it could be easily broken by addition of more hydrochloric acid to the system.

Several laboratory-scale demonstrations of the decladding flow-sheet shown in Fig. 1 have been made with simulated unirradiated fuel pins containing pellets 94% of theoretical density and with both unirradiated and irradiated pellets only 80% of theoretical density.

Fig. 1— Flowsheet for decladding and dissolution of Consolidated Edison fuel by the Darex-Thorex Process.

Fig. 2— Darex-Thorex flowsheet for total dissolution of Consolidated Edison fuel.

Fig. 3—Dissolution rate of stainless steel in boiling HCl-HNO₃. Dissolution time: 15 min

Fig. 4—Effect of chloride concentration on depassivation of 304L stainless steel in dilute aqua regia. Specimens in contact with titanium. Passivation treatment: 1 hr reflux in 15 M HNO₃-0.3 M CrO₃.

In all cases dissolution of the stainless steel in boiling 5 M HNO_3 --2 M HCl was complete in 3 hr, yielding a solution containing 50 g of stainless steel per liter. Uranium losses to the decladding solution with pellets 80% of theoretical density were between 0.1 and 0.5% irrespective of burnup of up to 575 Mwd/t (Table 2). With pellets of 94% of theoretical density, uranium losses were less than 0.05%. In a series of 25 cyclic experiments,⁹ where simulated fuel pins containing pellets of 80% of theoretical density were dissolved one-by-one according to the decladding flowsheet shown in Fig. 1 uranium losses also varied randomly from 0.1 to 0.5%.

The best dissolvent for thorium and thorium oxide that can be used in a titanium or a stainless steel dissolver is fluoride-catalyzed nitric acid, the Thorex process dissolvent.⁷ Dissolution rates were optimum with a 200% stoichiometric excess of 13 M HNO_3 --0.04 M NaF .⁶ The rate of reaction with this reagent containing 0.1 M $\text{Al}(\text{NO}_3)_3$ decreases with increasing pellet density; after a 5-hr digestion with 200% excess of acid the amount dissolved was 93, 81, and 75% for pellets of 94, 84, and 81% of theoretical density (Fig. 5). With pellets that were 94% of theoretical density, 26 hr was required for complete batch dissolution. It is anticipated that boron will be present in the dissolvent to aid in criticality control. With pellets of density 81% of theoretical, the presence of 0.1 M H_3BO_3 in the dissolvent had no effect on the rate of dissolution (Fig. 5, Curve A). Aluminum, which is present in the dissolvent to inhibit corrosion by fluoride ion, causes a decrease in the amount of pellets (81% of theoretical density) dissolved in 1 hr from about 55 to 35% as its concentration increases from zero to 0.4 M (Fig. 6).

Because of the low rate of dissolution of high density ThO_2 - UO_2 pellets, several alternative dissolvents were briefly investigated. The best reagent found was 13 M HNO_3 --0.04 M NaF containing 0.5 M $\text{Fe}(\text{NO}_3)_3$ or its equivalent of stainless steel nitrates. In a 200% excess of boiling reagent, the amount of 95.8% ThO_2 --4.2% UO_2 pellets (94% of theoretical density) dissolved in 1 hr increased to a maximum of 44% as the $\text{Fe}(\text{NO}_3)_3$ concentration increased from 0 to 0.5 M (Fig. 6). It is because of the enhanced rate of dissolution in the presence of iron that a total dissolution technique such as outlined in Fig. 2 is feasible.

Preliminary data indicate that irradiation to 575 Mwd/t has no effect on the rate of core dissolution.

Fig. 5—Effect of density and H_3BO_3 concentration on the rate of dissolution of 96% thorium oxide-uranium oxide fuel pellets in boiling 13 M HNO_3 —0.04 M NaF —0.1 M $\text{Al}(\text{NO}_3)_3$. Acid excess: 200%.

Fig. 6—Effect of ferric nitrate and aluminum concentrations on the dissolution of 96% ThO_2 — UO_2 pellets in boiling 13 M HNO_3 —0.04 M NaF . Acid excess: 200%.

Table 2. Uranium Losses in Decladding of Simulated Consolidated Edison Fuel Pins by the Darex Process

Decladding reagent: boiling 5 M HNO_3 -2 M HCl

Decladding time: 1-3 hr

Pellets: 96% ThO_2 - UO_2

Run No.	Pellet Density, % of theoretical	Irradiation Level, Mwd/t	Losses, %	
			U	Th
1	81	0	0.42	0.04
2	81	0	0.29	0.02
3	81	0	0.34	0.006
4	81	575	0.17	--
5	95	0	0.03	0.003
6	95	0	0.05	0.004

3.1.2 Dissolution of Consolidated Edison Fuel by the Sulfex Process.

The Sulfex process,⁶ in which stainless steel-clad fuel is declad with boiling sulfuric acid, is an alternative method for processing of Consolidated Edison type fuels. Decladding is achieved in 3 hr in a 200% excess of boiling 6 M H_2SO_4 before the ThO_2 - UO_2 core is dissolved in 13 M HNO_3 --0.04 M NaF --0.1 M $\text{Al}(\text{NO}_3)_3$ (Fig. 7). On the basis of laboratory experiments with unirradiated high-density (94% of theoretical) fuel pellets, uranium losses to the decladding solution of less than 0.1% can be expected even if the uranium is present as an oxide with an O/U ratio of 2.4. Ultimately, the decladding solution must be diluted to at least 4 M sulfate to prevent precipitation of stainless steel sulfates when the solution is cooled to room temperature.⁹ Since, in the plant, the process will be semicontinuous, the solution will probably be diluted shortly after the reaction has been initiated, i.e., clad dissolution will be initiated with 6 M H_2SO_4 and continued with 4 M H_2SO_4 . The only advantage in this technique is the less severe corrosion of the expected dissolver material, Ni-o-nel, and the lower uranium losses to the decladding solution. Details of the semicontinuous core dissolution technique for high-density fuel pellets have not yet been worked out. There are clear indications, however, that a minimum of a 200% excess of reagent will be required and that the dissolution time will exceed 20 hr. Dissolution of the core pellets after a Sulfex decladding will probably proceed somewhat more slowly than after Darex decladding because of the diminution of rate caused by traces of sulfate in the dissolvent (see below).

Disadvantages of the Sulfex-Thorex process are: the large volumes of hydrogen gas evolved during the decladding; the potentially large effects of cross-contamination of solutions on both decladding and core dissolution, e.g., passivation of stainless steel caused by nitrate; and the difficulty in recovering uranium from the waste decladding solution if losses are excessively high. With nonoxidized stainless

Fig. 7—Sulfex-Thorex dissolution of Consolidated Edison reactor fuel.

steel, as little as 0.01 M nitrate can cause passivation of 304 stainless steel in 6 M H_2SO_4 ; and, if the surface of the stainless steel has already been subjected to oxidizing conditions, e.g. by autoclaving or soaking in concentrated nitric acid containing Cr(III), the maximum tolerable nitrate concentration in 6 M H_2SO_4 may be as low as 0.0005 M.¹⁰ In plant operation it seems advisable to add 0.1 M formic acid to the sulfuric acid to assure destruction of any nitrate not removed by washing, and sparging with an inert gas may be required to remove gaseous nitrogen oxides from the system. Preliminary tests indicate that passivation in a nitrate-free system probably will not be a problem with freshly cut or brazed stainless steel fuels.¹⁰

Dissolution of 1 mole (55 g) of an 18-8 stainless steel results in the evolution of about 1.1 moles of H_2 :

With a 200% stoichiometric excess of boiling acid, the initial dissolution rate increases from about 2 to 29 mg/min·sq cm as the acid concentration increases from 2 to 8 M (Fig. 8). (The rates in mg/min·sq cm may be converted to mils/hr by multiplying by 2.94.)

The effect of $\text{ThO}_2\text{-UO}_2$ pellet density and particle size on uranium losses to boiling 6 M H_2SO_4 is illustrated in Fig. 9. With pellets containing about 96% ThO_2 , having a density (9.4 g/cc) 94% of theoretical, losses are less than 0.1% even after 24 hr exposure. The effect of the uranium valence state on losses is not discernible with pellets of greater than 90% of theoretical density. Pellets of lower density (81% of theoretical) containing UO_2 lost about 0.5% of their uranium in only 10 hr exposure (Fig. 9, curve D). The increase of loss with decreasing size of high-density (9.4 g/cc) pellets does not appear to be as serious as first anticipated, since it varied in 6 hr only from 0.03 to 0.16% as the particle size decreased to 100 mesh. During irradiation it is expected that pellet break-up will correspond roughly to a -4+8 sieve cut, in which case losses could well be less than 0.1% particularly since the presence of actively dissolving stainless steel tends to suppress dissolution of the uranium.

Several laboratory-scale flowsheet (Fig. 7) demonstrations were performed with simulated Consolidated Edison fuel pins containing irradiated and unirradiated pellets of densities 81 and 94% of theoretical. With pellets of density 81% of theoretical uranium losses were between 0.1 and 0.5% and were unaffected by burnups up to 445 Mwd/t (Table 3). With unirradiated fuel specimens containing pellets of density 94% of theoretical, the uranium losses were less than 0.05% (Table 3). Twenty-five simulated Consolidated Edison fuel pins were dissolved consecutively by the Sulfex-Thorex flowsheet,⁹ leaving any residue to the next cycle. Pellets were 95.5% $\text{ThO}_2\text{-U}_3\text{O}_8$, 81% of

Fig. 8—Initial dissolution rates of type 304L stainless steel in a 200% stoichiometric excess of boiling sulfuric acid. Dissolution time: 5 min.

Fig. 9—Effect of time, density, and particle size on uranium losses when unirradiated sintered 96% $\text{ThO}_2\text{-UO}_2$ pellets were exposed to boiling 6 M H_2SO_4 (5 ml per gram of pellets).

theoretical density. In all runs dissolution of the stainless steel cladding was initiated with a 200% excess of boiling 6 M H_2SO_4 ; in the last 15 cycles, the decladding solution was diluted to 4 M sulfate after about 40% of the stainless steel had dissolved. Uranium losses to the decladding solution varied randomly from 0.1 to 0.9% over the 25 cycles; however, the losses were proportional to the amount of heel remaining from the preceding core dissolution step (Fig. 10). The presence of a heel results from the reduced rate of core dissolution when traces of sulfate are present in the dissolvent.

With pellets of density 94% of theoretical, an increase in sulfate concentration in 13 M HNO_3 --0.04 M NaF--0.1 M $\text{Al}(\text{NO}_3)_3$ from 0 to 0.1 M caused a reduction in the amount dissolved in 1 hr from 32 to 6.5% (Fig. 11). With 13 M HNO_3 --0.04 M NaF--0.5 M $\text{Fe}(\text{NO}_3)_3$ the amount of pellets dissolved in 1 hr decreased from 42 to 13% as the sulfate concentration increased from zero to 0.1 M. In the presence of sulfate, an impervious coating [presumably $\text{Th}(\text{SO}_4)_2$] forms on the surface of the pellets and causes the lower rates of reaction. This problem may be avoided by careful washing after decladding.

Table 3. Uranium Losses in Decladding of Simulated Consolidated Edison Fuel Specimens by the Sulfex Process

Decladding solution: boiling 6 M H_2SO_4
Decladding time: 1-3 hr

Run No.	Pellet Density, % of theoretical	Irradiation Level, Mwd/t	Losses, %	
			U	Th
1	81	0	0.04	0.008
2	81	0	0.12	0.011
3	81	0	0.21	0.041
4	81	0	0.18	0.053
5	81	47	0.34	--
6	81	318	0.44	--
7	81	403	0.32	--
8	81	445	0.071	--
9	94	0	0.01	0.003
10	94	0	0.04	0.005
11	94	0	0.02	0.02
12	94	0	0.04	0.01

Fig. 10—Uranium loss to 6 M H_2SO_4 decladding solutions as a function of weight of $\text{ThO}_2\text{-U}_3\text{O}_8$ heel from preceding core dissolution. Pellet density: 80% of theoretical; 42 g of pellets per change.

Fig. 11—Effect of sulfate concentration on the dissolution of 96% thorium oxide-uranium oxide pellets in a 200% stoichiometric excess of boiling 13 M HNO₃-0.04 M NaF containing either iron or aluminum.

3.2 Class II: Stainless Steel--clad Uranium Oxide Core Fuels

Class II fuels have uranium oxide cores enclosed in stainless steel tubes. Alternative dissolution processes are the Darex in which the fuel may be completely dissolved in dilute aqua regia, and the Sulfex, in which the stainless steel is dissolved in dilute sulfuric acid and the core in nitric acid. Both processes have been developed on a small scale and will be evaluated in pilot plant operations. The following discussions use the Nuclear Ship Savannah Fuel (NSS) to illustrate the flowsheets and chemical variables. The data should be applicable to other fuels of this class with minor changes. Similarly, enriched uranium fuels clad in stainless steel, e.g. the APPR, can be processed by the Darex method.¹¹⁻¹⁵ The development work reported in the following sections was performed largely on unirradiated fuel samples. Data are now being obtained on irradiated samples.

3.2.1 Dissolution of Nuclear Ship Savannah Fuel by the Darex Process. The Darex process consists of three steps: (1) dissolution with dilute aqua regia in titanium equipment; (2) chloride removal to prevent corrosion of stainless steel in the solvent extraction and waste storage systems; and (3) adjustment of the nitrate solution to solvent extraction feed conditions. These steps may be accomplished continuously, semicontinuously, or in batch operations. Nitric acid concentrations ranging from 61 to 95 wt % HNO_3 can be used to volatilize the chloride.¹²

The ORNL Darex reference flowsheet for processing NSS fuel is shown in Fig. 12. Semicontinuous dissolution is accomplished by charging a batch of elements to the dissolver and continuously feeding 5 M HNO_3 --2 M HCl to the dissolver, which discharges by overflow to the feed adjustment tank. The remaining steps in the process are carried out in the feed adjustment tank. When the entire batch of dissolution product has accumulated, a quantity of dilute mixed acid is distilled off to remove excess water. Recycle nitric acid, 12 M HNO_3 containing a trace of chloride, is then added continuously while a mixed acid stream is distilled from the tank for return to the dissolution step. Fresh 61% HNO_3 is added in batches and the solution is refluxed with air sparging to volatilize the remaining chloride. True countercurrent action is achieved in that fresh 61% acid is added before the last chloride removal step. After the refluxing, the acid is distilled and collected for use in the next run. Only the addition of water to the product is required to adjust both the nitric acid and metal concentrations to the levels desired for solvent extraction feed. The times required for total dissolution and chloride removal are about 4 and 10 hr, respectively.

In the continuous dissolving of a nonhomogeneous fuel such as the N.S. Savannah, three distinct periods of dissolution occur. In the first period only stainless steel of known area is dissolved. The continuous dissolution rate of stainless steel in 5 M HNO_3 --2 M HCl increases directly with increasing F/S ratio* while the concentration

*Ratio of acid feed rate in cubic centimeters per minute to surface area in square centimeters.

Fig 12—Darex reference flowsheet for Nuclear Ship Savannah reactor fuel.

of dissolved metals decreases (Figs. 13 and 14). The data also show that the presence of 5.5% UO_2 , as in the case of APPR fuel which contains highly enriched uranium, does not affect the dissolution rate of stainless steel.¹⁵ The third period involves only the dissolution of UO_2 after all the stainless steel has been dissolved. In the second dissolution period, from the penetration of the clad until its total dissolution, stainless steel and UO_2 are dissolved simultaneously, with the area of either almost impossible to define. During this period the dissolver product stream is characterized by a buildup of uranium concentration to 120 g/liter, accompanied by a gradual drop in the stainless steel loading (Fig. 15). Stainless steel dissolution was complete in about 1 hr and uranium dissolution about 70% complete in 2 hr.

Chloride is removed from the dissolution product by distillation, using additional nitric acid to increase the volatility of the hydrochloric acid. Equilibrium data for the system $\text{HNO}_3\text{-HCl-H}_2\text{O}$ ⁵ show that hydrochloric acid is more volatile than nitric acid and that the relative volatility of the hydrochloric acid increases with increasing nitric acid concentration. True equilibrium cannot exist under flowsheet conditions due to decomposition reactions, but the trend persists. In the mixed acid recovery step, as 12 M HNO_3 is added and mixed acid is removed continuously at the same rate, the chloride concentration quickly reaches a maximum and declines while the nitric acid concentration increases toward the feed acid concentration (Fig. 16). The nitric acid concentration of the metals-bearing solution also increases and approaches an equilibrium value determined by the concentration of metallic nitrates in the solution.

After the chloride volatilization and recovery step, the remaining chloride is removed by refluxing at high nitric acid concentration with an air sparge. Higher nitric acid concentrations, longer reflux times, and air sparging promote chloride removal¹⁶ (Figs. 17 and 18). After chloride removal, only removal of the excess nitric acid and dilution with water are necessary to produce solvent extraction feed. The acid is removed by a single stage batch distillation. Figure 19 shows the concentration of the nitric acid overhead and the decrease in the free nitric acid concentration of the solution as the batch distillation proceeds.

A prototype fuel pin containing 41.5 g of UO_2 and 21.0 g of 304L stainless steel, irradiated to 1000 Mwd/t and decayed about 4 months, was processed as a batch operation in glass laboratory-scale equipment by the Darex Reference Flowsheet for Nuclear Ship Savannah reactor fuel (Fig. 12). The clad was penetrated in 10 min, but a total of 90 min was allowed for complete dissolution of the UO_2 pellets. The total time required for both dissolution and chloride removal was 6 hr.

More than 99.94% of the gross beta and rare earth activities and 99.63% of the ruthenium remained in the dissolver product solution during the Darex head-end treatment (Table 4). Ruthenium was expected to become

Fig. 13—Dissolution rate as a function of acid feed rate to surface area ratio for an acid feed 5 M HNO₃-2 M HCl.

Fig. 14—Dissolver product metal loading as a function of ratio of acid feed rate to surface area for acid feed 5 M HNO₃-2 M HCl.

Fig. 15—Continuous dissolution of simulated Nuclear Ship Savannah fuel. Acid: 5 $\underline{\text{M}}$ HNO_3 —2 $\underline{\text{M}}$ HCl fed at a rate of 1 ml/sq cm of initial surface area per minute.

Fig. 16—Composition of condensate during mixed acid evaporation at constant volume; 12 $\underline{\text{M}}$ HNO_3 added at same rate condensate collected. Initial solution: 83 g of stainless steel and 180 g of uranium per liter, 5 $\underline{\text{M}}$ HNO_3 and 2.2 $\underline{\text{M}}$ HCl ; 307 liters.

Fig. 17—Darex dissolver product chloride concentration as a function of reflux time for various initial nitric acid concentrations. Conditions: 100 g/liter APPR metal loading; updraft condenser; no sparging; initial chloride concentration 0.58 M; boilup rate/liquid volume ratio = 1/150 per hour

Fig. 18—Darex dissolver product chloride concentration as a function of reflux time for various initial nitric acid concentrations using an air sparge. Conditions: 100 g/liter APPR metal loading updraft condenser; initial chloride concentration 0.58 M; boilup rate/liquid volume ratio = 8.5/1 per hour.

Fig. 19—Nitric acid concentrations in the liquid and condensate during final evaporation of Darex dissolver solution. Initial conditions: 9.6 M HNO₃, 50 g of stainless steel per liter ($U/SS = 2.2$), trace chloride.

volatile at pot acidities of 8-11 M, but only 0.37% was volatilized and condensed with the recycle acids, and the bulk would thus be recycled to the dissolution step in a semicontinuous Darex process. Material balances were excellent between the initial dissolver solution and the final feed solution with the exception of zirconium-niobium, only 57% of which appeared in the final feed solution. Since only 0.003 and 0.03% of the total gross beta and gamma activities, respectively, were trapped in the caustic off-gas scrubbers, it was concluded that the zirconium-niobium activity was precipitated on the surfaces of the equipment. About 13% was actually recovered by boiling 6 M H_2SO_4 in the dissolver. Since the amount of activity trapped in the off-gas scrubbers was so low, the Darex process apparently does not impose a serious off-gas disposal problem.

Table 4. Fission Product Distribution during Darex Chloride Removal

Activity	Amount, % of Total			
	In Dissolver Product	In Re-covered Acids	In Feed	In Off-Gas Scrubber
Gross β	100	0.055	99.94	0.003
Gross γ	100	0.043	66	0.035
Zr-Nb β	100	0.029	57 ^a	0.043
Ru β	100	0.366	99.63	0.002
Rare earth β	100	0.47	99.95	0.002

^aAdditional 13% found after dissolver boiled with 6 M H_2SO_4 .

3.2.2 Dissolution of Nuclear Ship Savannah Fuel by the Sulfex Process. The Sulfex process is an alternative to the Darex method for reprocessing of stainless steel--clad uranium oxide fuels. A typical fuel, the Nuclear Ship Savannah, is declad in 3 hr in a 200% excess of boiling 6 M H_2SO_4 before the UO_2 core is dissolved in 10 M HNO_3 (Fig. 20). Passivation, the necessity for diluting the decladding solution to at least 4 M sulfate and the effect of the semicontinuous dissolution method expected in the plant were discussed in Sect. 3.1.2. At this time, an accurate estimate of the uranium losses to the decladding solution cannot be made. In tests with unirradiated fuel pins containing intact UO_2 pellets, uranium losses were about 0.005%; however, losses were as high as 0.05% with irradiated specimens (800 Mwd/t or higher) in which the UO_2 had shattered (Table 5). The higher losses with specimens irradiated to greater than 800 Mwd/t are attributed solely to the increase of surface area on fragmentation since the uranium loss was independent of irradiation level with specimens containing intact pellets.

Fig. 20—Sulfex process for decladding Nuclear Ship Savannah reactor fuel.

The principal advantage of the Sulfex process, if losses are low, is the decrease in volume of high-level radioactive wastes since the cladding material is separated from the fission product--bearing core prior to solvent extraction and can be stored as an intermediate level radioactive waste. Although the losses were acceptable at the 1440 Mwd/t level, it must be determined if more severe shattering (and hence higher losses) occurs in fuels irradiated at higher power densities to burnups of 7000 Mwd/t or greater. Average burnups of 7000 to 10,000 Mwd/t are expected for the Nuclear Ship Savannah and similar fuels such as the Yankee Atomic fuels.

One encouraging result of the radioactive-cell experiments is the fact that the rate of uranium loss to a typical decladding product solution containing 35 g of stainless steel per liter was only 0.04% per hour under a nitrogen blanket even though the UO_2 was fragmented (Fig. 21, lower curve). With pure 6 M H_2SO_4 under a nitrogen blanket, the rate of loss was 0.3% per hour. The need for an inert blanket after decladding is apparent since the rate of loss to the typical decladding solution increased to 0.81% per hour when air was used as the blanket gas. The very high rate in the latter case is attributed to the formation, in air, of iron(III) which is a good oxidant for UO_2 .

Table 5. Uranium and Plutonium Losses during 2 hr Decladding with Boiling 6 M H_2SO_4 of Irradiated Nuclear Ship Savannah Prototype Fuel Pins

Irradiation, Mwd/t	Losses, %		Pellet Form
	U	Pu	
0	0.005		Intact
250	0.003	0.006	Intact
450	0.003	0.04	Intact
650	0.003	0.01	Intact
800	0.005	0.02	Fragments
1000	0.03	0.03	Fragments
1440	0.045	0.052	Fragments

3.3 Class III: Stainless Steel--clad Sodium-bonded Fuels

The stainless steel cladding will be removed mechanically from all sodium or sodium-potassium bonded fuels and the liquid bond destroyed by reaction with steam in the mechanical processing head-end facility.¹⁷ The cores will then be sealed in 31-mil-thick aluminum cans to prevent the spread of radioactivity during transfer to the chemical dissolver, which is located in a separate building. Therefore each flowsheet in the following sections starts with the removal of the aluminum can by dissolution in caustic.

Fig. 21—Uranium losses under miscellaneous de-cladding conditions. Fragmented UO_2 pellets irradiated to 1040 Mwd/t; De-cladding solution, 6 M H_2SO_4 containing 35 g of stainless steel per liter.

In initial planning, it was assumed that the stainless steel jacket and fluid bond would be dissolved directly in the Darex or Sulfex acids. Calculations showed that the amount of heat and gas produced by the rapid reaction of small amounts of sodium would not be significant in comparison to the concurrent metal dissolution reactions. A number of Darex and Sulfex dissolutions were carried out on 12-in.-long x 4-in.-o.d. pins that contained 5.5 g of sodium between a stainless steel jacket and a glass rod core. In each case flashes of light were observed as the sodium reacted. Initially it appeared that the violent reaction could be successfully contained in process equipment. However, a detonation occurred in a later Darex experiment which shattered the 4-in. glass pipe used as a dissolver. Evaluation of the factors indicated that the detonation was probably caused by reaction of hydrogen and nitrogen oxides rather than by the direct reaction of sodium. It was concluded that neither Sulfex nor Darex should be considered for direct dissolution of sodium-bonded fuels until the safety of the system was assured after extensive experimental work.

3.3.1 Dissolution of Sodium Reactor Experiment I Fuel in Nitric Acid. The flowsheet for dissolving SRE-I slugs uses well developed technology¹⁸ and offers no new problems other than those associated with criticality control for slightly enriched uranium (Fig. 22). The aluminum can is dissolved in a mixture of sodium hydroxide and sodium nitrate. In the presence of sodium nitrate the evolution of hydrogen is suppressed in favor of the production of ammonia. The evolution of gases is at a practical minimum when conditions approximate the equation

The evolution of hydrogen approaches a minimum of 3 ml per gram of aluminum dissolved if the concentration of sodium nitrate in the dissolver solution does not fall below about 100 g/liter (1.2 M). This effect is apparently independent of caustic concentration. The dissolution or penetration rate of aluminum increases with caustic concentration from 1.5 mm/hr with 5% NaOH to 5 mm/hr with 10% NaOH and 13 mm/hr with 15% sodium hydroxide at the boiling point. If the initial caustic concentration exceeds 10%, the rate of reaction becomes too rapid for easy control in the plant. Uranium and plutonium losses are low in solutions up to 30% caustic but become appreciable at 50% caustic.

Dissolving conditions are fixed at mole ratios of 1/1.65/1.47 for Al/NaOH/NaNO₃ based on final solution stability, gas evolution, and reaction rate. The sodium nitrate is added first, followed by 18 M NaOH at a rate consistent with the heat and gas removal capacities of the dissolver. After aluminum dissolution is complete, the solution is jetted to waste and the cores and dissolver washed with water. Total can dissolution time is estimated as about 8 hr.

The amount of nitric acid required to dissolve uranium metal varies from 2.5 to 5.5 moles nitric acid per mole of uranium depending on the efficiency of the condenser system for converting NO₂ and NO to nitric

Fig. 22—Dissolution of SRE 1 core.

acid. In actual practice, starting with 9.0 M HNO_3 the existing ORNL system with an updraft condenser uses about 4.0 moles of nitric acid per mole of uranium. The nitric acid consumption could be decreased to 2.5 to 3.0 by the installation of a downdraft condenser into which air or oxygen is introduced to oxidize NO to NO_2 . The dissolution rate for uranium metal varies from about 35 mg/min·sq cm in 13 M HNO_3 to about 1 mg/min·sq cm in 1 M $\text{UO}_2(\text{NO}_3)_2$ -1 M HNO_3 . The rate increases with nitric acid and uranyl nitrate concentration.¹⁸ Total dissolution time for 0.75-in.-dia rods is estimated as about 8 hr with a 100% heel, i.e., with an equal amount of uranium metal remaining in the dissolver from a previous dissolving.

3.3.2 Dissolution of Sodium Reactor Experiment II Fuel in Nitric Acid. The aluminum can will be removed by caustic dissolution as described in Sect. 3.3.1 and the core dissolved in 13 M HNO_3 catalyzed by fluoride (Fig. 23). The technology for this dissolution step is well developed and little additional development work is required.^{18,19} It differs from the procedure used recently for dissolving thorium metal fuel in the Thorex process¹⁹ in that the aluminum can is removed in a separate step rather than being dissolved concurrently with the thorium in nitric acid. Based on previous pilot plant experience, the loss of thorium and uranium to the decladding solution will be >0.1%.

The dissolution rate of thorium metal varies from 130 mg/min·sq cm in boiling 13 M HNO_3 containing 0.05 M fluoride as a catalyst to ~1.0 mg/min·sq cm in 1 M $\text{Th}(\text{NO}_3)_4$ --6 M HNO_3 --0.05 M F.¹⁸ Acid consumption amounts to about 5 moles of nitric acid per mole of thorium metal. The total dissolution time for the 0.75-in.-dia core is estimated as about 8 hr in 13 M HNO_3 --0.04 M F--0.04 M Al with a 100% metal heel in the dissolver. The aluminum is added to the dissolvent to complex the fluoride and lower the corrosion rate. The aluminum in the can is not dissolved concurrently with the core in this case, i.e., it is not used to complex fluoride, since aluminum must be present in the solution fed to the dissolver in any event to prevent corrosion of the process feed line.

3.3.3 Dissolution of Consumers Public Power Fuel I in Nitric Acid. The aluminum can will be removed from the CPPD-I core, 90% U-10% Mo alloy, by dissolution in caustic as described in Sect. 3.3.1. As with other fuels having a sodium bond, the stainless steel will probably be removed mechanically and the core recanned in aluminum. After decladding, in which uranium losses are expected to be less than 0.1%, the core is dissolved in 5 hr in a volume of boiling 11 M HNO_3 sufficient to produce a solution containing 260 g of uranium per liter (Fig. 24).²⁰ About 95% of the molybdenum precipitates as H_2MoO_4 during core dissolution, with the solubility of molybdenum in the product solution being about 0.013 M. The volume of the solid, after centrifugation, is about 20% of the original volume of nitric acid. The solid is washed with 1 M HNO_3 to remove uranium before being dissolved in a 200% stoichiometric excess of hot 5 M NaOH. Less than 0.1% of the uranium is lost to the caustic solution. If washing is done carefully, essentially no uranium is left

Fig. 23—Dissolution of SRE II core.

Fig. 24—Dissolution of Consumers Public Power fuel in nitric acid.

in the solid; however, if a significant amount of uranium was present, it would remain after the caustic treatment as insoluble sodium diuranate. The diuranate can be dissolved in 11 M HNO_3 and the resulting solution used as the core dissolvent for the next batch of fuel. Dissolution tests on irradiated fuel specimens are now in progress to determine the fate of plutonium.

The principal advantage of this process is the separation of molybdenum from uranium prior to solvent extraction. Consequently, the solvent extraction raffinate can be evaporated to a volume of 65 gal per ton of uranium processed, which is 1/18 the volume of waste when the iron-nitric acid dissolution process is used (Sect. 3.3.5). If precipitation is slight in the evaporated waste, the wastes can probably be stored as acidic solutions in the cooled high-radioactive-level stainless steel waste tanks. If precipitation is serious, iron could be added to the waste to complex and solubilize the molybdenum, or the waste could be combined with iron-bearing acidic Darex wastes.

The major disadvantage is the necessity for separating relatively large amounts of solid molybdic acid by centrifugation. The molybdic acid is a fine, slow-settling precipitate which is easily removed by centrifugation. However, if the engineering problems associated with solid-liquid separation prove to be excessive, the alternative dissolution method outline in Sect. 3.3.5 will be considered.

3.3.4 Dissolution of Consumers Public Power Fuel II in Nitric Acid. The Consumers Public Power reactor core II will consist of slightly enriched uranium monocarbide clad in stainless steel and bonded with sodium. Because of the sodium bond, this fuel probably will be declad mechanically. At this point, the sodium and carbide could be converted to the respective oxides by reaction with steam before dissolution in nitric acid. An alternative approach is the recanning of the UC in aluminum after mechanical removal of the stainless steel and sodium. Chemical removal of the aluminum with caustic during processing probably will result in excessive uranium losses because of the reactivity of the monocarbide with aqueous solutions. The only alternative is complete dissolution of the aluminum and core in the nitric acid. Before this method is attempted, it will be necessary to determine if an explosion hazard exists. Conceivably, violent vapor-phase reactions could occur between nitrogen oxides and carbon-containing gases produced by hydrolysis of the carbide. A thorough study of these and other problems associated with the processing of this fuel has been initiated.

3.3.5 Dissolution of PRDC Blanket Fuel in Nitric Acid--Ferric Nitrate. The aluminum can will be removed from the PRDC blanket rods, depleted 97% U-3% Mo, by caustic dissolution as described in Sect. 3.3.1. Two reagents for complete dissolution of the core alloy in nitric acid are being studied, ferric and phosphate ions, to complex molybdenum as soluble heteropolymolybdates.^{21,22} The use of nitric acid-ferric nitrate as the dissolvent is the preferred method at present (Fig. 25). In this case, the volume of waste is of less concern

Fig. 25—Dissolution of PRDC blanket fuel in nitric acid-ferric nitrate.

than for the CPPD-I fuel (Sect. 3.3.3) since it is less radioactive and will be stored as intermediate-level waste rather than as high-level waste.

According to data obtained at HAP0,²¹ an iron concentration of 0.5 M is necessary if a stable solvent extraction feed solution is to be obtained which contains 1.0 M uranium without having a terminal H⁺ concentration greater than 3 M. Dissolution of 92% uranium-8% molybdenum alloy in 5 M HNO₃ containing iron is rapid; the rate increased almost linearly from 10 to 90 mg/min·sq cm as the ferric nitrate concentration increased from 0 to 0.75 M (Fig. 26). Rates were no higher in solutions containing greater than 0.75 M Fe(NO₃)₃. The advantage of this process is the elimination of precipitates from the system; however, because of the large quantity of iron required to complex the molybdenum, very high volumes of high radioactive level wastes are generated, i.e., 328 gal per ton of uranium processed for 97% uranium-3% molybdenum alloy and 1175 gal per ton of uranium processed for 90% uranium-10% molybdenum alloy (based on concentrating to 25 g of molybdenum per liter).

The iron--nitric acid dissolution method was selected for processing of the blanket fuel because the low irradiation level will permit storage of the waste in the large intermediate-level waste tanks (Sect. 5.0). Pilot plant comparison of the relative merits of the nitric acid (Sect. 3.3.3) and the iron--nitric acid dissolution methods will be of value.

3.4 Class IV: Aluminum-clad Enriched Uranium-Aluminum Alloy Core Fuels

Foreign Research Reactor fuel consists of uranium-aluminum alloy plates clad with aluminum and brazed into a box assembly with an over-all composition of 84% aluminum, 15% uranium (20% enriched), and 1% silicon. Dissolution of uranium-aluminum alloy proceeds rapidly and smoothly in mercury-catalyzed nitric acid (Fig. 27). The solvent extraction flow-sheet specifies a feed composition of 1.2 M Al(NO₃)₃--1 M HNO₃. Tests with prototype fuel plate showed that dissolution with 7.5 M HNO₃--0.005 M Hg(NO₃)₂ yields a dissolver solution containing 1.5 M Al(NO₃)₃ and 1.3 M HNO₃. Over-all dissolution time is estimated as 8 hr.

3.5 Class V: Aluminum-clad Thorium-core Fuels

Aluminum-clad thorium fuels will be reprocessed by removing the clad with caustic and dissolving the core in nitric acid catalyzed by fluoride. The Borax-IV fuel is unique in that the bond between the oxide pellets and the M-388 (1% nickel--99% aluminum) alloy cladding is metallic lead.²³ For reasons based mainly on the low solubility of lead nitrate in concentrated nitric acid and the high Al/Th mole ratio, 6.5, in the fuel, dissolution is best accomplished by a method in which the cladding and bond are removed in separate steps prior to core dissolution (Fig. 28).²⁴ Aluminum in the cladding alloy is first dissolved by the standard caustic decladding method.¹⁸ Decladding is achieved in what corresponds to boiling 2 M NaOH--1.78 M NaNO₃ (NaOH/Al mole ratio = 1.65).

Fig. 26—Dissolution rates of 91.6% uranium-8.4% molybdenum alloy in boiling 5 M HNO₃ containing Fe(NO₃)₃. Dissolution time: 5 min HNO₃/U mole ratio: 4.

Fig. 27—Dissolution of Foreign Research Reactor fuel

Fig. 28—Decladding and dissolution of Borax IV fuel.

Actually, water and 3.6 M NaNO_3 are added to the dissolver, and then the appropriate amount of 18.8 M NaOH is added continuously to effect the dissolution. The uranium loss in this step is expected to be less than 0.07%. Next, the lead bond and nickel are dissolved in boiling 2 M HNO_3 (HNO_3/Pb mole ratio of 4) resulting in an additional uranium loss of about 0.2%. Finally, the $\text{ThO}_2\text{-UO}_2$ core is dissolved in a 200% stoichiometric excess of boiling 13 M HNO_3 --0.04 M NaF --0.1 M $\text{Al}(\text{NO}_3)_3$. This flowsheet will be tested on fully irradiated fuel samples early in 1960.

Conditions given for the dissolution of the aluminum cladding are those found to be optimum in the development of a reprocessing method for aluminum-clad production reactor fuels; similarly, conditions for dissolution of the lead bond had to be selected so that the waste volume and uranium loss to the solution were minimized. Fortunately, both objectives were met when the lead was dissolved in dilute nitric acid. The solubility of lead nitrate in nitric acid at 26°C decreases from 1.5 to 0.007 M as the nitric acid concentration increases from 0 to 12 M (Fig. 29). The presence of thorium in the solution causes a further depression of the lead solubility. Lead dissolves at rates of 3 to 20 mg/min.sq cm in 0.5 to 2 M HNO_3 (Table 6) according to the reaction

Several laboratory-scale flowsheet demonstration experiments were performed under the conditions shown in Fig. 28. Uranium losses in the two decladding steps were less than 0.23% (Table 7).

Obvious alternative methods which were considered for reprocessing the Borax-IV fuel are (1) total dissolution in mercury-and fluoride-catalyzed nitric acid, (2) removal of the aluminum jacket with caustic followed by dissolution of the lead and core in fluoride-catalyzed nitric acid, and (3) removal of the clad and bond in mercury-catalyzed nitric acid prior to normal Thorex core dissolution. With the high (6.5) Al/Th mole ratio in the fuel, total dissolution is recognized to be impractical because of the low solubility²⁵ of aluminum nitrate in the concentrated nitric acid required for core dissolution. Removal of only the aluminum during decladding is impractical because lead, in addition to its insolubility in concentrated nitric acid, seriously retards the rate of core dissolution.²⁴ The presence of lead also causes a decrease in the rate of dissolution of aluminum in mercury-catalyzed nitric acid; however, dissolution of aluminum in the presence of the appropriate amount of lead (Al/Pb mole ratio of 8.77) is sufficiently rapid in boiling 4 M HNO_3 if the mercuric nitrate concentration is 0.5 M (Fig. 30). It has been estimated²⁶ that \$11,000 worth of mercury would be required to declad the Borax-IV fuel in this way. This cost might not prohibit use of the third possible method since the Borax-IV core is the only fuel that contains metallic lead. Certainly, the use of 0.5 M $\text{Hg}(\text{NO}_3)_2$ is impractical in an economical, long-range, process for similar fuels.

Fig. 29—Solubility of lead nitrate at 25°C in HNO_3 – $\text{Th}(\text{NO}_3)_4$ solutions as a function of HNO_3 and $\text{Th}(\text{NO}_3)_4$ concentration.

Fig. 30—Effect of mercury concentration on the rate of dissolution of aluminum in boiling 4 M HNO_3 in the presence of lead. Al/Pb mole ratio = 8.77; HNO_3 /Al mole ratio = 4.0. Aluminum specimens were right cylinders, 0.95 cm diameter, 2.5 cm high.

Table 6. Initial Rates of Dissolution of Lead Foil in Dilute Nitric Acid

Dissolution time: 10 min
Temperature: boiling point

HNO_3 Conc., <u>M</u>	Initial HNO_3/Pb Mole Ratio	Rate, mg/min·sq cm
0.5	2	3.1
	3	3.3
	4	3.3
	6	3.7
1.0	2	7.7
	3	9.3
	4	9.5
	6	12.2
1.5	2	11.0
	3	13.2
	4	16.5
	6	17.8
2.0	2	13.1
	3	15.9
	4	19.5

Table 7. Uranium and Thorium Losses in Dissolution of Borax-IV Fuel by the Two-step Decladding Method

Aluminum dissolved in 2 M NaOH-1.78 M NaNO_3 ; 2 hr
Lead dissolved in 2 M HNO_3 ; 1 hr

Run No.	Losses, %					
	During Al Dissolution		During Pb Dissolution		Over-all	
	U	Th	U	Th	U	Th
1	0.028	0.004	0.088	0.0003	0.116	0.0043
2	0.032	0.004	0.083	0.030	0.115	0.0034
3	0.063	0.006	0.16	0.010	0.223	0.016
4	0.022	0.006	0.061	0.007	0.083	0.013

3.6 Class VI: Zirconium-Uranium Alloy Fuels

The EBWR is a typical example of low-enriched uranium-zirconium fuel whereas the STR and PWR seed are representative of highly enriched fuel. Dissolution problems with this type of fuel stem from the impractically low rate of dissolution of zirconium in nitric acid, the explosive reactions of uranium-zirconium or uranium-niobium alloys with nitric acid in the absence of fluoride,^{27,28} and the corrosive action of mixtures of hydrofluoric and nitric acid on materials of construction. The Modified Zirflex process was developed to eliminate or minimize these problems.²⁹ The procedure that will probably be used to process EBWR fuel is shown in Fig. 31, route b. Ammonium fluoride is used to dissolve both the Zircaloy-2 jacket and alloy core. The zirconium is soluble, but uranium, niobium, and tin precipitate as $(\text{NH}_4)\text{UF}_5$, $(\text{NH}_4)_2\text{NbF}_7$, and metallic tin. Aluminum nitrate and nitric acid are then added to dissolve the uranium precipitate and the tin to produce a solution suitable for recovery of uranium and plutonium by solvent extraction with tributyl phosphate. The niobium oxide, which forms on acidification, is insoluble in nitric acid and must be removed by filtration or centrifugation and discarded. About 0.03% of the uranium is lost with the niobium. The aluminum acts as a salting agent in the extraction system and also reduces corrosion by complexing fluoride. The use of ammonium fluoride as the dissolving agent eliminates the explosion hazard since nitric acid is not added until dissolution of the alloy is complete. Corrosion is also minimized since ammonium fluoride is compatible with austenitic stainless steels and aluminum is added at the moment of acidification. Complete dissolution of the EBWR fuel requires about 28 hr.

In an alternative process (Fig. 31, route a), ammonium hydroxide is added to the ammonium fluoride dissolver solution to precipitate hydrous zirconium oxide and metathesize the solid NH_4UF_4 and $(\text{NH}_4)_2\text{NbF}_7$ to hydrous oxides. The hydrous oxides are separated from the fluoride solution by settling or centrifugation and washed with ammonium hydroxide. The precipitates readily dissolve in nitric acid to yield a solvent extraction feed containing about 1.4 M U and a F/Zr mole ratio of about 2. Since the fluoride is strongly complexed at this F/Zr ratio, no aluminum ion need be added as a fluoride complexing agent. As the filtrate and washes are recycled, after evaporation, for use as dissolvent, no uranium is lost. The volume of the solvent extraction feed by route (a) is only 1/20 that of with (b). However, further engineering feasibility tests are required to evaluate the problems in the solid-liquid separation and metathesis steps before this flowsheet can be used in the pilot plant. Tests on irradiated fuel samples are in progress to determine the fate of plutonium.

The over-all dissolution of EBWR fuel is a maximum when the concentration of ammonium fluoride is 6 M.²⁹ The dissolution rate of Zircaloy-2, the EBWR jacket, in 6 M NH_4F at the boiling point is very rapid initially, 15 mg/min·sq cm, but decreases to essentially zero as the F/Zr mole ratio in solution approaches 6 (Fig. 32). Similarly, the

Fig. 31—Modified Zirflex processes for dissolution of high uranium (EBWR-core) fuel with ammonium fluoride solutions.

Fig. 32—Dissolution of zirconium alloys in 6 M NH_4F .

dissolution rate of EBWR core alloy, 93.5% U--5% Zr--1.5% Nb, decreases from about 5 mg/min·sq cm to essentially zero as the mole ratio of fluoride to total metal in the dissolver product changes from 100 to 6. Consequently, the over-all fluoride to metal ratio chosen for the dissolution reaction was 6.5. Under these conditions the over-all dissolution rate is about 3 mg/min·sq cm. Actually, it appears that the rate is limited by the formation of a solid $(\text{NH}_4)_2\text{NbF}_7$ film on the alloy in the later stage of dissolution.

3.7 Class VII: Aqueous Solution or Slurry Fuels

Aqueous solutions of enriched uranyl sulfate and slurries of ThO_2 or $\text{ThO}_2\text{-UO}_2$ in water from the Homogeneous Reactor will be processed as they become available. Since the Homogeneous Reactor is an experimental reactor, it is difficult to assign a definite composition to the burned fuel. The following composition for one core solution is based on 50% on-stream time for 2 years at 5 Mw:

UO_2SO_4	12.3 kg
Fe_2O_3	trace
Cr_2O_3	trace
ZrO_2	trace
$\text{Ni}(\text{SO}_4)_2$	2.4 kg
H_2SO_4	2.0 kg
Fission products	1.8 kg

The heavy water is removed and about 25 gal of natural water added prior to transfer to the pilot plant. The solids will be separated from the solution by centrifugation and discarded. If they contain a significant amount of uranium, they will be dissolved in 10 M H_2SO_4 in a tantalum lined tank or in 13 M HNO_3 --0.04 M F in a titanium tank. These solutions would be blended with the initial clear solution. Extraction would be accomplished by a TBP-25 flowsheet designed for that purpose,³⁰ using 2.5% TBP-Amsco. The aqueous solution is diluted with nitric acid to optimum extraction conditions.

Thorium oxide slurries would be dissolved and extracted by methods similar to those shown in Sects. 3.1 and 4.1, respectively, for Consolidated Edison type fuel.

4.0 SOLVENT EXTRACTION PROCESSES

Most of the solvent extraction processes listed in the following sections are in the development stage. Consequently, the conditions and results quoted do not necessarily represent the optimum.

4.1 Extraction of Consolidated Edison Fuel by the Acid Thorex and Acid Interim-23 Processes

The Acid Thorex and Acid Interim-23 solvent extraction processes were developed³¹ to recover thorium and uranium from thorium-bearing fuels (Table 1). These processes have been tentatively selected for use in the pilot plant as the first and second cycles, respectively, rather than the conventional Thorex¹⁹ process because they do not require aluminum as a salting agent and consequently produce an order-of-magnitude smaller volume of highly radioactive waste. The disadvantages of these processes are a factor of 10 lower decontamination factor for ruthenium in the Acid Thorex process and the use of a new diluent, Decalin, rather than Amsco. Limited data indicate that the Decalin (decahydronaphthalene) system has a stage height in the extraction section approximately twice that for the Amsco system. However, the columns in the pilot plant are thought to be long enough to obtain the necessary uranium and thorium recovery. An additional disadvantage is that two solvent concentrations will be required, 42.5% and 5% TBP, for the two cycles, necessitating more complicated solvent.

An Acid Thorex first cycle flowsheet for Consolidated Edison, a representative thorium-bearing fuel, is shown in Fig. 33. The Acid Thorex first cycle uses a feed containing 1.5 M $\text{Th}(\text{NO}_3)_4$, 0.085 M $\text{UO}_2(\text{NO}_3)_2$, 4.0 M HNO_3 , 0.04 M fluoride, and 0.1 M aluminum; a scrub containing 2 M HNO_3 , 0.003 M PO_4^{3-} , and 0.01 M ferrous sulfamate; and an extractant containing 42.5% TBP-Decalin. The thorium extraction factor at the feed plate was 2 and in the scrub section greater than 4 when the flow ratio of feed to extractant to scrub was 1 to 5 to 1. Five extraction and eight scrub stages were used in countercurrent batch extractions. In laboratory-scale experiments, the thorium loss to the raffinate was less than 0.1%; decontamination factors from rare earths, zirconium-niobium, and ruthenium were greater than 10^4 , 500, and 35, respectively, with a gross gamma decontamination factor of ~ 200 . This decontamination factor is satisfactory for thorium, since tentative thorium specifications require a thorium decontamination factor of 100. This will allow the thorium product to be stored in intermediate-level storage tanks as part of the second cycle raffinate waste.

The second cycle Interim-23 flowsheet uses 5% TBP in Amsco to extract only the uranium, leaving the thorium with the remaining fission products (Fig. 34). The Acid Interim-23 second cycle has a feed containing 1.5 M $\text{Th}(\text{NO}_3)_4$, 0.08 M $\text{UO}_2(\text{NO}_3)_2$, 0.1 M $\text{Al}(\text{NO}_3)_3$,* 0.04 M NaF ,* and less than 0.5 M HNO_3 ; a scrub containing 5 M HNO_3 ; and an extractant containing 5% TBP-Amsco. The uranium extraction factors were about 2 at the feed plate and >5 in the scrub section using a feed to extractant to scrub volume ratio of 1 to 2 to 0.4. Six extractant and eight scrub

*The aluminum nitrate and sodium fluoride would be present only when the Interim-23 flowsheet is used as a first cycle.

Fig. 33—Solvent extraction of Consolidated Edison fuel by the Acid-Thorex process.

Fig. 34—Solvent extraction of Consolidated Edison fuel by the Acid-Interim 23 process.

stages were used in countercurrent batch extractions. In laboratory-scale experiments the uranium loss to the raffinate was about 0.01% and the uranium separation factor from thorium was about 10^3 . Decontamination factors for rare earths, zirconium-niobium, and ruthenium were consistently $>10^5$.*

Tentative uranium product specifications have been determined as follows: The activity of the uranium product will increase rapidly as a result of the growth of daughters of U-232, particularly Tl-208 which has a gamma energy of 2.6 Mev. One year after the removal of these daughters, Tl-205 will contribute about 10^9 γ c/m/g U-233 or about 3×10^8 γ c/m/g total uranium. Tentative uranium product specifications have been set which require that the fission product activity should not exceed the activity of these daughters after one year. The solvent extraction feed will contain about 10^{13} rare earth γ c/m/g U, 2.5×10^{13} Zr-Nb γ c/m/mg U, and 2.5×10^{12} Ru γ c/m/mg U. Decontamination factors from total rare earths, zirconium-niobium, and ruthenium of 2.5×10^5 , and 2.5×10^4 , respectively, will be required to meet these specifications. Data obtained in the two-cycle tests show that a decontamination factor of 10^7 should be obtained for the uranium stream. This will meet the requirements for Consolidated Edison fuel. It should be emphasized that a large amount of additional development work is required to optimize the Acid Thorex conditions.

The Interim-23 process can be used as a first cycle and a TBP-25 process for the second cycle if there is no interest in recovering thorium. However, this choice increases the volume of the high-activity waste by a factor of 15 since the thorium will be present in this waste rather than in the intermediate-activity second cycle waste. The conditions for the TBP-25 flowsheet are well known.³⁰

4.1.1 Feed Adjustment. The dissolver solution may be adjusted to Acid Thorex solvent extraction feed conditions by evaporating to a boiling temperature of 125°C then diluting with water. If the Interim-23 flowsheet is to be used in the first cycle, the dissolver solution will be evaporated to a boiling temperature of 135°C before dilution (Fig. 35). At a boiling point of 125°C the solution will be 2.5 M $\text{Th}(\text{NO}_3)_4$ and 5.5 M H^+ , which upon dilution with 0.7 volume of water will give an Acid Thorex feed solution containing 1.5 M $\text{Th}(\text{NO}_3)_4$ and 4 M HNO_3 . At a boiling point of 135°C the solution will be 3.5 M $\text{Th}(\text{NO}_3)_4$ and 1.5 M H^+ , which upon dilution with 2 volumes of water will give an Acid Interim-23 feed solution containing 1.2 M $\text{Th}(\text{NO}_3)_4$ and 0.5 M H^+ .

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*Two cycles could not be made consecutively in the laboratory experiments because of the high level of activity which would be required for first cycle feed in order to have a sufficient amount of activity in the second cycle product for accurate analysis. Separate feeds were therefore used in each cycle.

Fig. 35—Evaporation of Consolidated Edison core solution for extraction feed adjustment.

4.1.2 Homogeneous Neutron Poisons. One of the means of criticality control which may be used during the dissolution and fuel adjustment cycles is the addition of soluble neutron poisons to the fuel solution. These neutron poisons must be separated from the fuel in the solvent extraction cycle. The solubility and volatility of boron, cadmium, and rare earth elements during the dissolution and feed adjustment steps and the separation of the fuel from the neutron poisons have been determined.³² A single solvent extraction cycle by the Interim-23 flowsheet gave decontamination factors from boron, rare earths, and cadmium of 3×10^3 , $<3 \times 10^3$, and <500 , respectively. Countercurrent batch extractions have not been made to determine the decontamination factors with the Acid Thorex flowsheet. Distribution coefficients in 50% TBP-Amsco, however, indicate that separation from boron and the rare earths will be adequate. Additional data will be required to determine the separation from cadmium when high concentrations of TBP are used.

4.2 Extraction of Consolidated Edison Fuel by the Darex-Thorex and Darex-Interim-23 Processes

The Darex-Thorex and Darex-Interim-23 processes are being developed to extract uranium and thorium from nitrate solutions containing large amounts of stainless steel. Such solutions could be formed during the decladding of Consolidated Edison type fuels (Class I, Table 1) by the Darex process (Sect. 3.1.1). Although laboratory studies with high-density oxide pellets have indicated that the loss of uranium to the decladding solution will be $<0.1\%$, solvent extraction systems are being developed to recover the fuel from this solution in case such fuel loss is excessive in pilot plant operations. The most promising procedure for processing this solution that has been developed is to combine the clad solution with the core solution or to use the clad solution to dissolve the core (Fig. 2), and extract both the thorium and uranium by a Darex-Thorex flowsheet or extract the uranium from the thorium and fission products by a Darex-Interim-23 flowsheet. These flowsheets will be similar to those shown in Figs. 33 and 34 with the exception that the aqueous feed will contain up to 70 g of stainless steel per liter, the nitric acid concentration will be lower in the Thorex flowsheet and the TBP concentration in the Interim-23 flowsheet may be 2.5%.

Total dissolution of Consolidated Edison type fuel by Darex head end step yields a solution which can be concentrated to 1.25 M $\text{Th}(\text{NO}_3)_4$, 110 g/liter stainless steel, and 0.5 M HNO_3 (Fig. 36). Since ferric nitrate is approximately equivalent to aluminum nitrate as a salting agent, the addition of aluminum will not be required in the Darex-Thorex flowsheet. In laboratory batch countercurrent extraction experiments, under the conditions shown in Table 8 for a Darex-Thorex flowsheet, thorium was decontaminated from zirconium-niobium and ruthenium by factors of 300 and 20, respectively, with a thorium loss of $<0.1\%$. Similarly, uranium was decontaminated from zirconium-niobium and ruthenium by factors of $>2 \times 10^3$ and $>2 \times 10^4$ with the Acid Interim-23 flowsheet conditions (Table 9). The uranium loss was $<1\%$. Total rare earth decontamination factors were not determined in this initial

development work since they are always $>10^4$. It therefore seems likely that with further development, uranium and thorium decontamination and recovery will be adequate by these flowsheets.

4.2.1 Feed Adjustment. The feed solution for the Darex-Thorex and Darex-Interim-23 flowsheets are both about 1.25 M Th, 110 g/liter stainless steel, and 0.5 M HNO_3 ; therefore the adjustment of the combined core and clad solutions will be the same for either flowsheet. In a single experiment starting with a solution 0.56 M thorium, 0.91 M stainless steel, 0.04 M uranium, 7.9 M H^+ , and 0.02 M cadmium, evaporation of the solution to a boiling point of 135°C and dilution resulted in a feed with the composition 1.25 M thorium, 1.35 M stainless steel, 0.086 M uranium, 0.043 M cadmium, and 0.6 M H^+ (Fig. 36).

Considerable difficulty is encountered if the acidity of the stainless steel-bearing solution is reduced below a still-to-be-determined minimum concentration. In the absence of thorium the solutions froth vigorously and "bump" at boiling temperatures of 130 - 135°C . This frothing seems to be due to the decomposition of the iron nitrate to oxide and could possibly be avoided by preventing localized heating of the solution. When thorium was present no frothing was noted, but precipitation of iron oxide was observed when the temperature of the solution exceeded about 137°C . Freshly precipitated oxide may be redissolved in acid, but redissolution of oxide that has been heated to higher temperatures is very difficult.

4.2.2 Homogeneous Neutron Poisons. Studies have not been made of the separation of the neutron poisons from the fuel when stainless steel is present in the feed. Data³² from aluminum nitrate--salted solutions, however, demonstrated that boron and rare earth elements may be satisfactorily separated from the uranium and thorium by using either the Interim-23 or the Thorex flowsheets. Cadmium separation was always satisfactory with the Interim-23 flowsheet but is extracted from highly salted aqueous solutions by 42.5% TBP.

Table 8. Darex-Thorex Flowsheet Conditions for the Extraction of Thorium and Uranium from Stainless Steel Solutions

Feed	1.25 M Th, 0.07 M U, 2 M SS, 0.5 M HNO_3 , 0.04 M F
Scrub	2 M HNO_3 , 0.003 M PO_4 , 0.01 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$
Extractant	42.5% TBP-Amsco
Flow Ratio	Feed/extractant/scrub = 1/5/1
Stages	5 extraction, 8 scrub

Fig. 36—Evaporation of combined Consolidated Edison core and decladding solution for extraction feed adjustment.

Table 9. Darex-Interim-23 Flowsheet for the Extraction of Uranium from Thorium-containing Stainless Steel Solutions

Feed	1.25 M Th, 0.07 M U, 2 M SS, 0.5 M HNO ₃ , 0.04 M F
Scrub	5 M HNO ₃ , 0.003 M PO ₄ , 0.01 M Fe(NH ₂ SO ₃) ₂
Extractant	2.5% TBP-Amsco
Flow Ratio	Feed/extraction/scrub = 1/4/8
Stages	6 extraction, 5 scrub

4.3 Extraction of Nuclear Ship Savannah Fuel by the Darex-Purex Process

The Darex-Purex solvent extraction process is applicable to all class II fuels (Table 1) that are dissolved by the Darex method. It is also applicable to enriched fuels containing stainless steel such as the APPR.¹⁴ A Darex-Purex first cycle flowsheet for processing Nuclear Ship Savannah fuel, a representative fuel of this class, is shown in Fig. 37. The plutonium level in this fuel is expected to be about 2800 g per ton of uranium. Plutonium is first converted to Pu(IV) by the addition of nitrite, and then both the uranium and plutonium are extracted with 30% TBP in Amsco diluent and scrubbed and stripped in pulsed columns.

Uranium and Pu(IV) are separated from the iron, chromium, nickel, and fission products in the feed stage of the extraction section; they are further separated in the scrub section where the solvent is back-washed with 3 M HNO₃. The loaded solvent is cascaded to the strip column where it is stripped with 0.01 M HNO₃. The aqueous product is concentrated by evaporation, adjusted with nitric acid, and again treated with nitrite prior to the second cycle. The plutonium and uranium are co-extracted again in the second cycle and finally separated from each other in a third cycle by a standard Purex^{33,34} operating procedure.

The aqueous waste stream from the first cycle contains more than 99.9% of the fission products and stainless steel as nitrate salts. The over-all uranium decontamination factors required for the NSS fuel are 3×10^6 for gross β and 1.5×10^7 for gross γ ; those for plutonium are 10^6 for gross β and 5×10^6 for gross γ .

Table 10 summarizes data for uranium and Pu(IV) extraction and stripping by this flowsheet.³⁵ Results from batch countercurrent experiments show that adequate salting strength for the extraction of uranium and Pu(IV) is provided by the high concentration of stainless steel, 60 g/liter, as nitrate salts in the aqueous feed. With distribution coefficients of 12.2 for uranium and 4.0 for Pu(IV), <0.01% of the plutonium and uranium are lost in 2.5 and 6 theoretical extraction stages for uranium and Pu(IV), respectively. The distribution coefficients are lower in the scrub section but extraction is

Fig. 37—Solvent extraction of N. S. Savannah Reactor fuel by the Darex-Purex process.

satisfactory with a solvent/aqueous volume ratio of 13/3. As a result, reflux of uranium and Pu(IV) is limited to 8 and 17% in the scrub section. Based on previous experience with the Purex system, 6 to 8 scrub stages are recommended for maximum decontamination from fission products.

Table 10. Uranium and Pu(IV) Distribution in the First Solvent Extraction Cycle for Nuclear Ship Savannah Reactor Fuel

See Fig. 37 for conditions

	Distribution Coefficient (E_a^0)	Extraction Factor	No. of Theoretical Stages Required for 0.01% Loss
Extraction			
U	12.2	13.7	2.5
Pu(IV)	4.0	4.5	6
Scrub			
U	7.1	34.5	6-8 ^a
Pu(IV)	2.9	14.1	
Strip			
U	1.2	0.6	7
Pu(IV)	0.1	0.05	5

^a Estimated number of scrub stages needed to attain maximum decontamination for fission products.

The stripping operation is not highly efficient owing to the back-salting effect of uranyl nitrate. It is seen that the uranium distribution coefficient at the feed stage is 1.2. To overcome this unfavorable condition for stripping, a volume of aqueous strip twice that of the solvent is provided. Thus, with an extraction factor of 0.6, stripping to the desired loss level of 0.01% is accomplished in 7 theoretical stages. Conditions for stripping Pu(IV) are more favorable. Only 5 stages are required.

Because of the lack of irradiated fuel specimens for class II fuels, development work on irradiated fuels has been confined, until recently, to uranium dioxide--stainless steel specimens of APPR fuel irradiated to 40% U-235 burnup and decayed 2 years. Results showed that the Darex dissolution procedure and the presence of stainless steel in the solvent extraction system did not impair the efficiency of the TBP-25 process.^{14,35}

Gross β and γ decontamination factors across the first cycle using 5% TBP-Amsco were 5.4×10^5 and 7.4×10^4 , respectively (Table 11). The decontamination factors for ruthenium, 2.1×10^5 , and for zirconium-niobium, 3.6×10^4 , are particularly high when compared to the standard Purex process (30% TBP) which nominally shows 830 and 4×10^3 , respectively, for these activities in the first cycle.

Table 11. Fission Product Decontamination across First Solvent Extraction Cycle^{14,35}

Feed prepared by Darex dissolution process from sectioned APPR fuel plate of 40% U-235 burnup after 2 years decay

Activity	Decontamination Factor
Gross β	5.4×10^5
Gross γ	7.4×10^4
Ruthenium	2.1×10^5
Zirconium-niobium	3.6×10^4
Rare earths	1.7×10^7
Plutonium	430

4.4 Extraction of Nuclear Ship Savannah Fuel by the Purex Process

The standard Purex solvent extraction process will be used to recover pure uranium and plutonium from nitric acid feeds prepared from low-enrichment fuels that contain uranium but no significant amount of other metals. For example, the cores of the Nuclear Ship Savannah, and the SRE-1 will be processed by the Purex method when the cladding has been removed chemically or mechanically and the cores dissolved in nitric acid. The details of the Purex process are described elsewhere.^{33,34} In essence, the flowsheet is very similar to that shown in Fig. 37 except that stainless steel is absent and the concentrations of nitric acid in the feed and scrub are 2 and 3 M, respectively. The uranium and plutonium will be co-extracted in two cycles and separated in a third cycle. The plutonium will be isolated on an anion exchange column.

4.5 Extraction of 20% Enriched Foreign Research Reactor Fuel by the TBP-25 Process

Foreign Research Reactor fuel contains partially enriched uranium, 20% U-235, rather than the 93% U-235 used in other research reactors. Consequently, the Research Reactor fuel will contain a significant

amount of plutonium, 4 g per kilogram of uranium. The standard TBP-25 extraction flowsheet³⁰ was therefore modified to permit recovery of plutonium (Fig. 38). If the plutonium proves to be of little value, 0.03 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ will be added to the scrub solution of the first extraction column to reduce the plutonium to Pu(III) and direct it to the waste stream. The partitioning column will be omitted. Decontamination of the uranium is completed in a standard second solvent extraction cycle and a column of silica gel.^{13,36} A solvent composition of 6% TBP in Amsco diluent and an aqueous composition of 1.2 M $\text{Al}(\text{NO}_3)_3$ and 0.5 M HNO_3 were chosen for the first cycle of solvent extraction to obtain the maximum extraction efficiency consistent with criticality control. The uranium and Pu(IV) o/a distribution coefficients are about 10 times higher for 6% TBP than for 2.5% TBP (Table 12). Nitrite is added to convert plutonium to Pu(IV). The distribution coefficients for uranium and Pu(IV) are 19 and 4 under flowsheet conditions, which assures complete recovery of these elements in the extraction column. In the partitioning column, the remaining fission products and plutonium are removed from the organic phase by an aqueous scrub stream containing 0.03 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$, 0.75 M $\text{Al}(\text{NO}_3)_3$, and 0.5 M HNO_3 . The ferrous ion reduces Pu(IV) to Pu(III), a form not readily extracted by TBP. The presence of aluminum ensures the extraction of uranium. The use of pure nitric acid as a scrub solution was unsuccessful. The distribution coefficients for uranium and plutonium under flowsheet conditions were 1.15 and 0.04, respectively, but decreased to 0.05 and 0.003 in the absence of aluminum.

Table 12. Effect of Acidity and TBP Concentration on Uranium and Plutonium Extraction

Feed: 5.2 mg U/ml, 1 M $\text{Al}(\text{NO}_3)_3$, 10^6 Pu(IV) c/m/ml, varying HNO_3
 Solvents: 2.5 and 6% TBP in Amsco 125-82
 Equal-volume equilibrations for 3 min at 25°C

Feed Acidity, M	Uranium Eg		Plutonium(IV) Eg	
	2.5% TBP	6% TBP	2.5% TBP	6% TBP
0.5	2.74	20.0	0.28	2.52
1	2.43	17.1	0.42	3.83
2	1.79	12.0	0.65	4.99
4	1.04	6.1	1.03	6.79

Fig. 38—Solvent extraction of 20% enriched Foreign Research Reactor fuel.

Table 13. Fission Product Decontamination across First Solvent Extraction Cycle for Foreign Research Reactor Fuel^a

See Fig. 39 for conditions

Activity	Decontamination Factor
Gross β	8.4×10^4
Gross γ	1.5×10^4
Ruthenium	1.9×10^5
Zirconium-niobium	8.0×10^3
Rare earths	1.0×10^5

^aFeed prepared by mercury-catalyzed nitric acid dissolution of irradiated uranium-aluminum alloy fuel irradiated to 8% U-235 burnup and decayed 9 months.

Solutions prepared by dissolution of unirradiated prototype Foreign Research Reactor fuel and containing plutonium tracer were treated with gelatin, filtered through sand, and successfully processed in 0.75-in.-dia pulsed columns. All aqueous streams contained 0.05 M H_3BO_3 to aid in criticality control. Uranium losses to the aqueous waste, plutonium product, and stripped solvent streams with 22 ft of extraction column, 6 ft of back extraction in the partitioning column, and 11 ft of stripping column, were less than 0.001, 0.001, and 0.002%, respectively. Plutonium losses were 0.03% to the aqueous waste and 4.1% to the uranium-bearing solvent from the partitioning column with 8 ft of partitioning section in this column.

A reasonable estimate of fission product decontamination from uranium that may be achieved with the first cycle solvent extraction flowsheet developed for Foreign Research Reactor fuel is shown in Table 13. These decontamination factors were obtained in a 10-hr run in miniature mixer-settlers which provided 8 stages in turn for extraction, scrubbing, and stripping. Aqueous feed was prepared by mercury-catalyzed nitric acid dissolution of uranium-aluminum alloy fuel of 8% U-235 burnup and 12 months' decay. Gross beta and gross gamma decontamination factors of 8.4×10^4 and 1.5×10^4 , respectively, were obtained across the first cycle. Decontamination from ruthenium was excellent, 1.9×10^5 . Zirconium-niobium are the major contaminants found in the aqueous product from the first cycle, with a decontamination factor of 8×10^3 . The value of 10^5 for rare earths may be questioned, since decontamination factors of 10^6 to 10^7 from these activities is commonplace in TBP extraction processes.

4.6 Extraction of Zirconium-Uranium Alloy Fuel by the Modified Zirflex-Purex Process

Previous experience^{37,38} has demonstrated that uranium and plutonium may be extracted from solutions containing fluoride provided the fluoride is highly complexed (by aluminum or zirconium) and the nitrate concentration in the feed is high. At Idaho the uranium was extracted from a solution containing 0.0014 M U, 0.55 M Zr, 0.006 M Sn, 0.014 M Cr, 0.745 M Al, 1.1 M H⁺, 3.3 M F, and 2.24 M NO₃ with 10% TBP. In the ORNL Metal Recovery Pilot Plant plutonium was extracted from a solution containing 0.0011 M Pu, 1.22 M Mg, 0.28 M Al, 0.11 M Ca, 6 M H⁺, 0.023 M Si, 0.14 M F, and 9 M NO₃ with 30% TBP. Dissolution of the EBWR core I by the Modified Zirflex procedure gives a solution containing 0.074 M U, 0.8 M Al, 0.04 M Zr, 0.002 M Nb, 0.3 M NH₄, 3 M H⁺, 0.8 M F, about 5 M NO₃⁻, and varying amounts of plutonium. The uranium and plutonium can undoubtedly be extracted from this solution with 30% TBP by adding additional aluminum nitrate to complex the fluoride. Zirconium, niobium, and other fission products would be further removed by second and third solvent extraction cycles of a Purex type flowsheet. Since no development work has been done on this specific system, the degree of decontamination in the first cycle is unknown.

4.7 Extraction of Molybdenum-bearing Fuels by the Purex Process

Scouting experiments show that a Purex type solvent extraction system can undoubtedly be used to recover uranium and plutonium from molybdenum- and iron-bearing nitrate solutions.³⁵ The following experiments were performed on solutions obtained by dissolution of unirradiated fuel alloys by the conditions outlined in the flowsheets for the CPPD-1 core and PRDC blanket in Figs. 24 and 25. Plutonium nitrate was added to the dissolver product solutions so that the fate of both uranium and plutonium could be determined. Extensive testing with irradiated samples will be carried in further development work to determine decontamination factors and optimum operating conditions.

The test conditions used in batch countercurrent extraction experiments were

	<u>CPPD-1</u>	<u>PRDC-Blanket</u>
Aqueous feed	0.63 M U, 0.013 M Mo, 3.2 M H ⁺	1 M U, 0.074 M Mo, 0.5 M Fe, 2.75 M H ⁺
Relative vol.	100	100
Solvent	30% TBP	30% TBP
Relative vol.	155	253
Scrub	3 M HNO ₃	3 M HNO ₃
Relative vol.	31	51

Results of tests with 7 extraction and 5 scrub stages through 5 volume changes followed by batch stripping showed that the molybdenum had no adverse effect on solvent extraction and that the stage requirements were no greater than required for normal Purex operation (Sect. 4.4).

Analysis of the organic phase of the fourth scrub stage and the stripped aqueous uranium-plutonium product showed that separation from molybdenum was satisfactory. The concentration of molybdenum in these streams was below the limits of detection, i.e., <1 and <5 ppm, respectively.

4.8 Extraction of Uranium, Thorium, and Plutonium from Sulfex Decladding Wastes

Losses of uranium, thorium, and plutonium to Sulfex decladding solution (Sects. 3.1.3 and 3.2.2) are not expected to exceed $\sim 0.1\%$, particularly in the case of the high-density $\text{ThO}_2\text{-UO}_2$ pellets. However, processes are being developed to recover these values in case losses are excessive. The recovery process currently favored uses a primary amine as the extractant.³⁹ However, equipment required for this recovery system will not be installed in the pilot plant until the need is apparent.

5.0 WASTE STORAGE

Wastes from the ORNL pilot plant will be handled according to their health hazard level and their heat-generation level. Low level wastes are those that contain <1 microcurie/liter and can safely be discharged into White Oak Creek after holdup in the existing settling basin and treatment in the existing lime-soda plant. These low-level wastes include process water and other dilute streams which are not directly contaminated by the fuel reprocessing. The low-level wastes will not be considered further in this paper.

Intermediate level wastes are defined as those which are too radioactive to be discharged to the environment but which have heat generation rates low enough to permit storage in tanks that are not cooled internally, which may be either the existing concrete tanks or, if necessary, new concrete or mild steel tanks. These wastes include decladding wastes and solvent extraction raffinates from low- to medium-burnup fuels. All intermediate-level wastes will be neutralized prior to storage and will be decreased in volume by evaporation if the cost of this step is economically justified. There are now six 170,000-gal concrete tanks at ORNL. They contain some sludge left over from previous use and will require some checking and repiping (which may include piping of off-gas into existing stacks) before being used for semipermanent storage of reactor processing wastes. It has been estimated that a full concrete tank can safely dissipate 40,000-70,000 Btu/hr.^{40,41}

High level wastes defined as those generating too much heat to permit storage in the concrete tanks. These wastes will consist of first column solvent extraction raffinates and will be concentrated as far as practical by evaporation prior to storage. These wastes will be stored, without neutralization, in internally cooled stainless steel tanks. Three 15,000-gal tanks will be built, two for storage and one for standby. These tanks will be cooled with water circulating through internal coils and have a design heat removal capacity of 2.5×10^6 Btu/hr, each with the waste at 160°F and the inlet coolant water at 90°F.⁴²

5.1 Heat Generation Rate

Tables 14 and 15 list the fission-product heat generation rates for high- and intermediate-burnup fuels to be processed at ORNL. The initial rates were calculated for 180 days after discharge from the reactor, and the subsequent rates are shown at 1-year intervals thereafter. This division between high and intermediate levels was made arbitrarily on the basis that when the initial heat rate was less than 70,000 Btu/hr the waste would be stored in uncooled tanks. The totals in Table 14 show that all the listed high-level wastes could be stored in one of the stainless steel tanks if heat removal was the only consideration. The totals in Table 15 show that all the listed intermediate-level wastes could be stored in two or three concrete tanks if heat removal was the only consideration. The decladding wastes are not listed since they do not present a heat removal problem. Even a high loss (0.5%) in the decladding wastes for all the high-level fuels would not add a significant heat burden on the intermediate-level tanks.

5.2 Highly Radioactive Waste Volumes

Table 16 lists the expected high-level waste volumes based on the following assumptions:

Class I fuels

- (1) 32 tons of Consolidated Edison thorium, 4 tons of Rural Co-operative thorium.
- (2) 50% is chemically declad by Sulfex and processed by Acid-Thorex to produce 1300 gal of waste per metric ton of thorium; waste is decreased in volume by a factor of 20 for storage as acidic waste, 65 gal/ton of thorium processed.
- (3) 25% is chemically declad by Darex and processed by Acid-Thorex to produce 65 gal of acidic waste concentrate per ton of thorium.
- (4) 25% is dissolved by Darex and processed by Darex-Thorex to produce ~740 gal of acidic waste concentrate per ton of thorium. This waste contains ~100 g of stainless steel per liter.

Class II fuel

- (1) 21 tons of Nuclear Ship Savannah uranium.

- (2) 50% is chemically deacid by Sulfex and processed by Purex to produce 65 gal of acidic waste concentrate per ton of uranium.
- (3) 50% is dissolved by Darex and processed by Darex-Purex to produce 740 gal of acidic waste concentrate per ton of uranium.

Class III fuel

- (1) 24 tons of Consumers Public Power-1 uranium.
- (2) Mechanical removal of stainless steel cladding and sodium bond.
- (3) Nitric acid dissolution and removal of molybdenum in head end.
- (4) Processed by Purex to produce 65 gal of acidic waste concentrate per ton of uranium.

With these assumptions, the high-activity waste volumes total about 18,000 gal, less than the 30,000 gal total allowed for two 15,000-gal tanks in use and one in reserve. If just enough of these fuels were processed by Darex-type flowsheets to decrease the total waste-concentrate volume to 15,000 gal, all the wastes could be stored in one tank. (It was shown in Sect. 5.1 that the total waste heat generation rate from these fuels through 1965 will be less than the heat-removal capacity of one tank.) Such a change would leave another 15,000 gal of storage capacity for some of the higher activity fuels listed in Table 5.2 or for high activity fuels after 1965.

Table 14. Heat Generation of High-burnup Fuels after 180 Days' Decay and at 1-Year Intervals Thereafter to 1965

Reactor	Heat Generation Rate, Btu/hr					
	1960	1961	1962	1963	1964	1965
Class I						
Con. Ed. 1	--	--	--	1,060,000	455,000	293,500
Con. Ed. 2	--	--	--	--	--	1,060,000
Rural Coop. 1	--	--	91,000	36,150	21,900	15,600
Rural Coop. 2	--	--	--	--	91,000	36,150
Class II						
N. S. Savannah	--	--	--	--	156,000	72,800
Class III						
CPPD-1, 1/3 core	--	--	--	--	146,500	62,100
CPPD-1, 1/3 core	--	--	--	--	--	181,500
			91,000	1,096,150	870,400	1,721,650

Table 15. Heat Generation of Intermediate-burnup Fuels after 180 Days' Decay and at 1-Year Intervals Thereafter to 1965

Fuel	Heat Generation Rate, Btu/hr					
	1960	1961	1962	1963	1964	1965
Class III						
SRE-1	17,240	5,860	3,430	1,817	1,620	1,172
SRE-2	--	25,400	11,900	9,680	4,240	3,230
PRDC, Axial						
Blanket-1	--	--	3,090	747	426	213
PRDC, Axial						
Blanket-2,3	--	--	--	--	6,180	1,494
PRDC, Axial and Radial Blanket	--	--	--	--	--	44,390
Class IV						
Foreign Research	--	12,660	5,076	3,072	2,178	1,560
Reactor (6 cores)	--	--	12,660	5,076	3,072	2,178
"	--	--	--	12,660	5,076	3,072
"	--	--	--	--	12,660	5,076
"	--	--	--	--	--	12,660
Class V						
Borax-IV	--	2,890	825	413	41	--
Class VI						
EBWR-1	--	--	--	28,150	11,250	6,820
Class VII						
HRT core	--	a	a	a	a	a
	17,240	46,810	36,981	61,615	46,743	81,865

^aNot calculated, but expected to be well under 70,000 Btu/hr initially.

5.3 Intermediate-Activity Waste Volumes

Wagner⁴³ and Blomeke⁴⁴ have estimated that the total volume of intermediate-activity waste for all ORNL programs for the period 1960-65 is 408,000 gal of extraction raffinates and 724,000 gal of decladding solutions, not including the high-activity wastes listed in Table 16 but including wastes from other programs not considered in this paper. After neutralization this will yield about 1,300,000 gal of intermediate-activity wastes to be stored in tanks that are not cooled internally. Since the waste volume may exceed the capacity of the existing tanks,

the volumes will probably be decreased by evaporation before storage. Conger⁴³ has estimated that these intermediate-heat-level wastes might be evaporated to 73,000-102,000 gal of neutralized concentrate. The problems involved in evaporation of the neutralized decladding wastes have been studied previously,^{45,46} but additional work is required. Without volume decrease, as estimated by Wagner and Blomeke, the average sodium concentration is 2.2 M. If the wastes were concentrated by a factor of 2-3, the storage volumes would be decreased to 255,000-433,000 gal. Thus the total 1960-65 intermediate-activity neutralized wastes would be 328,000-535,000 gal, an amount that could be contained in existing concrete tanks.

Table 16. High-Activity Waste Volumes through 1965^a

Fuel	Volumes, gal		Total
	Purex or Acid-Thorex	Darex or Darex-Thorex	
Class I			
Con. Ed.	1560	5920	7480
Rural Coop	195	740	935
Class II			
N.S. Savannah	682	7770	8452
Class III			
CPPD-1	1560	--	1560
	3,997	14,430	18,427

^aSee text (Sect. 5.2) for assumptions.

The volume and composition of intermediate-activity wastes formed by the processing described in this report are shown in Table 17. The volumes and compositions shown are those that exit from the processes and do not reflect the effects of neutralization and evaporation. Further work is required to determine the optimum procedure for combining and evaporating these wastes before the final storage volume can be stated. It is obvious, for example, that the 51,000 gal of waste water can be re-used in the processes or evaporated, or perhaps even decontaminated in the low-activity treatment plant and discharged.

The volume of waste contributed by second solvent extraction cycle raffinates and alkaline solvent washing solutions are not included in

Table 17. Intermediate-Activity Waste Volumes^a

	Volumes, gal		
	Decladding Solutions	Wash Water	Extraction Raffinate
Con. Ed. (32 tons Th) and Rural Coop. (4 tons Th)			
18 tons, Sulfex decladding and Acid Thorex	22,167 ^b	18,097	c
9 tons, Darex decladding and Acid Thorex	22,141 ^d	5,603	c
9 tons, combined Darex-Thorex	---	---	c
N.S. Savannah (21 tons U)			
10.5 tons, Sulfex decladding and Purex	27,769 ^b	22,669	c
10.5 tons, combined Darex-Purex	---	---	c
CPPD-1 (24 tons U)			
All caustic declad, followed by molybdenum removal and Purex	1,772 ^e 8,719 ^f	1,132 ---	c c
SRE-1 (2.9 tons U)			
All caustic declad and Acid Thorex	193 ^e	123	3,770 ^g
SRE-2 (1.72 tons U + Th)			
All caustic declad and Acid Thorex	115 ^e	73	2,240 ^g
PRDC Axial and Radial blankets (49.1 tons U)			
All caustic declad and Fe-HNO ₃ core dissolution	3,690 ^e	---	63,900 ^g
Foreign Research Reactors (0.7 tons U)			
All processed by TBP-25	---	---	32,500 ^h
Borax-IV (0.32 tons U + Th)			
All caustic declad followed by lead removal and Acid Thorex	1,136 ^e 686 ⁱ	725 177	--- 416 ^g
EBWR-1 (5.5 tons U)			
All processed by Modified Zirflex	---	---	111,000 ^j
	88,388	50,914	213,826
Possible volumes after evaporation	(77,000)	353,128 (0)	(61,000)

^aSee text for assumptions (Sect. 5.2).^b100 g/l SS, 4 M H₂SO₄^cThese LAW streams are high level and their volumes are shown (after concentration) in Table 16.^d50 g/l SS, 3.1 M H⁺, 1.25 M Cl⁻, balance NO₃⁻^e2 M Al, 6.3 M Na, 1 M NO₃⁻, balance OH⁻^f0.8 M Na₂MoO₄, 3.3 M NaOH^gAssumed 1300 gal/ton^h1.2 M Al(NO₃)₃, 1 M HNO₃ⁱ0.4 M Pb, 0.5 M HNO₃^jBased on tentative, dilute-uranium feed flowsheet; may be much smaller after further development.

Table 17. These wastes do not contribute a significant heat generation rate and their volume is not expected to be critical under the following conditions: Concentration and recycling of second cycle aqueous raffinate to the first cycle, these wastes finally appearing as high-activity waste in many cases; and neutralization of intermediate-activity wastes with caustic and caustic carbonate wastes used for solvent washing, which would not significantly increase the amount of sodium ion that will appear as the result of normal neutralization operations. It is assumed that condensates from evaporation of neutralized wastes or from rectification of recovered acid will be of sufficiently low activity level that they can be discharged through the low-activity-waste lime-soda plant.

5.4 Fission Product Recovery from Wastes

A significant fraction of the higher-level waste streams may go to the ORNL Fission Product Pilot Plant (F3P) for radioisotope separation and recovery instead of directly to evaporation and storage. The F3P plant may take almost all the Purex-type first cycle wastes. The effect of isotope recovery is not included, however, in the preceding discussion on the heat generation rate and volume of wastes. Isotope recovery would materially decrease the heat-removal load but would not decrease the over-all waste volume since it must be assumed that the effluent from the F3P plant will be treated as intermediate-activity waste. The fission product recovery operation may actually increase the waste volumes since additional chemicals are added to the wastes in the recovery processes. For this reason, the Purex first cycle waste streams should be concentrated, before being sent to the F3P plant, to recover nitric acid that otherwise would return to the waste tanks as sodium nitrate.

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MECHANICAL PROCESSING OF SPENT POWER REACTOR FUEL AT
OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

The mechanical processing of spent power reactor fuels as an aid to or as a substitute for chemical head ends is being actively investigated by Oak Ridge National Laboratory in two development programs:

1. Underwater mechanical equipment program for the predissolution treatment of fuel to eliminate massive inert hardware and disassembly of fuel (if required) to facilitate processing of fuel on a production level in the Power Reactor Fuel Processing Pilot Plant now being erected.

2. Dry cave mechanical equipment program to determine the feasibility of dejacketing stainless steel-clad NaK- or Na-bonded fuels of uranium and uranium-molybdenum and of shearing (chopping) and leaching metallic-clad tubular fuel arrays of the oxides of uranium and/or thorium.

An underwater facility to receive, store, remove inert hardware, and disassemble and charge fuel to charger carriers has been designed and most of the features accepted for final design. Full-sized equipment, consisting of carriers, a traversing table, disassembly saw, hydraulic dejacketer, auxiliary dejacketer, slug washer, and slug canner for dejacketing and handling the stainless steel-clad NaK-bonded fuel of the SRE Core 1 has been built but is not yet evaluated. Disassembly, chopping and leaching tubular assemblies has been shown to be feasible in laboratory investigations. A prototype shear is being designed and full-scale batch and continuous leachers have been fabricated for testing.

MECHANICAL PROCESSING OF SPENT POWER REACTOR FUEL AT

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Oak Ridge National Laboratory is currently engaged in two mechanical processing programs for spent reactor fuel. These programs, which are of equal importance, are (1) underwater operation to facilitate the processing of fuel in the Power Reactor Fuel Processing Pilot Plant (PRFPPP) and (2) "dry cave" research and development to determine the feasibility of dejacketing metallic-clad NaK- and Na-bonded uranium and uranium-molybdenum fuels and the chopping and leaching of metallic-clad fuels of uranium and/or thorium oxides.

1.0 MECHANICAL PROCESSING OF FUEL UNDERWATER

Spent fuel shipped*** to the PRFPPP will be unloaded, stored, mechanically processed, and placed in charging casks by operations carried out entirely underwater. There are no shielded dry caves to supplement this procedure. The fuel is received in compartmented shielded casks (up to 75 tons) in canisters or baskets or with a suitable handling device to permit unloading, transportation, and subsequent underwater storage by suspension from a support rail located above the surface of the water. Normally, mechanical operations will be performed on the various fuels only after they have been stored and scheduled for processing in the chemical head end cells.

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*** See Sect. 3.0 of paper by H. E. Goeller in this volume.

Once the cover has been removed in a conventional manner from a shipping cask placed in the 20 x 20 x 35 ft deep portion of the canal (Fig. 1 and 2) each fuel assembly is removed by a 1-ton crane and transported to one of the two storage areas (25 ft wide by 36 ft long) and stored on the appropriate storage rail. In the event of a fuel assembly rupture during shipping (as shown by cooling water analyses), it will be canned in aluminum, prior to storage, by a simple canning device located in the unloading pit.

Each type of fuel is stored as a single assembly in containers which are placed side by side on storage rails. The storage rails, 24 in. apart, are transverse to the long axis of the canal and are subtended by a 3- to 5-ft-wide aisle running the full length of the canal. Access to each storage rail is by a 1-ton traveling crane moving along this aisle. Compartments 1-ft wide filled with water are located between storage rails to prevent a critical event occasioned by fuel in transit being inadvertently brought between fuel in storage. Interlocks on the 1-ton overhead personnel-carrying cranes limit the direction of travel in the rail storage area to a direction parallel to the rails and "raise" and "lower" to minimize the probability of dropping a fuel basket by collision caused by actuating the crane in the wrong direction.

1.1 Disassembly

The underwater mechanical facility which receives fuel from the storage canals has two main functions. In it fuel shipped in canisters, such as the sodium-bonded Power Reactor Development Corporation and Consumers Public Power Development fuel and solution or slurry fuels is decanned, and inert metal end adapters of all fuel are removed. In some cases the removal of inert end adapters causes disassembly of the fuel without additional mechanical operation. A third function, disassembly or actual splitting of fuel assemblies into smaller tube bundles, can be accomplished, if the need arises, by the use of hand tools (Sect. 2.2.1). Likewise, any custom cutting or pre-solution preparation not normally associated with the various fuel types would be accomplished with improvised hand tools. Spent fuel types to be mechanically processed and the planned mechanical operation that will be executed on each type are presented in Table 1. In the case of the NaK-bonded SRE fuels, dejacketing is carried out in air in a different facility (Sect. 2.1) and the fuel is recanned to accomodate conventional wet processing techniques. For PRDC and CPPD fuels the method to be used is not yet obvious. Although chemical methods* appear risky at this time, they have not been

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* See paper by R. E. Blanco et al. in this volume.

Fig. 1—PRFPPP Spent fuel receiving and handling facilities.

Fig 2—Elevation of unloading and charging pit and dissolver cell

Table 1. Mechanical Processing Operations Planned
for Various Spent Fuels

		Underwater Mechanical Operation ^a			
		Canister Opening	Removal of Inert End Adapters	Disas- sembly	Sheath or Jacket Removal
Stainless steel-clad high-en- richment UO ₂ -ThO ₂ core	Consolidated Edison	--	--	--	--
	Rural Coop	--	X	--	--
Stainless steel-clad low-en- richment UO ₂ core	Nuclear Merchant Ship Savannah	--	X	X ^b	--
Stainless steel-clad NaK or Na- bonded U or ceramic core	Sodium reactor Exp. 1 (low- enrichment U)	X	X	X ^b	X ^c (R&D)
	Sodium reactor Exp. 2 (high- enrichment U- Th alloy)	X	X	X ^b	X ^c (R&D)
	PRDC blanket, CPPD-1 (high- enrichment U-Mo core)	X	X	X ^b	--; X (R&D)
Al-clad en- riched U-Al alloy core	Foreign Research reactors	--	--; X	--	--
Al-clad Th metal or ceramic core	Borax IV (Al- clad Pb-bonded enriched UO ₂ -ThO ₂)	--	--	--	--

Table 1. Mechanical Processing Operations Planned
for Various Spent Fuels (continued)

		Underwater Mechanical Operation ^a			
		Canister Opening	Removal of Inert End Adapters	Disas- sembly	Sheath or Jacket Removal
Zircaloy-clad Zr-U alloy core	EBWR (Zr-2-clad low enriched U-Zr-Nb-alloy core)	--	--	--	--
Stainless steel-clad enriched U-SS sintered core	APPR, Northern States Super- heater (R D only)	--	X	--	--
Aqueous solu- tion or slurry	HRT core solution, UO ₂ SO ₄ , or blanket slurry ThO ₂	X	--	--	--

a. -- = operation not normally required; X = required; X (R&D) = for research and development purposes.

b. A natural consequence of removing the end adapters.

c. In air.

abandoned. Limited quantities of these fuels may be dejacketed in air solely on a research and development basis to establish other possible methods of processing.

1.1.1 Underwater Sawing

It appears possible to carry out the two main mechanical operations, opening of canisters and removal of inert end adapters, by a simple underwater saw (Fig. 3). This saw, which is located under 10 ft of water on one wall of the deep unloading pit of the canal, is capable of clamping a canister or fuel assembly and of making transverse cuts as required. Longitudinal cuts do not at present appear to be a requirement. An air-operated hacksaw and bandsaw were selected over other abrasion disk saws to do the cutting because of the high horsepower required for the underwater operation of the abrasion disk.

The procedure for operating the saw, including particulate collection and disposal of inert hardware removed, is:

1. Place canister or fuel assembly on receiving step of saw in near-vertical position with the 1-ton personnel-carrying crane.
2. Actuate air clamps to clamp entire object and raise saw rails to horizontal position. This position is fixed at a depth of 10 ft of water to always give safe shielding to operating personnel.
3. Locate saw at appropriate location for removal of canister lid or inert end adapter by actuating the dolly positioning mechanism. Actuate independently air-operated saw clamps to seize work locally to avoid binding and breaking of saw blades. Location of cut to remove end adapters is such that end caps are not loosened to liberate core materials.
4. Make saw cut at an appropriate speed of the air-driven motor dependent upon the metal being cut. Continue cuts, as required, as described previously.

1.1.2 Particle Collection

Particles produced by the saw are collected by a sloping tray (not shown). From underneath the tray, water is withdrawn from a low point centrally located. Tray effluent is passed through a settling tank and discharged through a filter and returned to the canal or sent to a radioactive drain depending on the success of particle removal. It is expected that the particle size range will be from 2 to 200 mean particle diameter.

Fig. 3—Underwater disassembly equipment.

Large objects, such as portions of canisters and inert end adapters, will be picked up by manipulators and dropped into underwater shielded collection containers for disposal when filled.

1.2 Method of Charging to a Dissolver

Once an assembly has been properly cropped by the saw, the saw rails are lowered to the original near-vertical position and an ice tong type lifting device is attached to one end, picked up, and placed in a simple frame wire holder for bottom loading into a charger cask (Fig. 2). The same holder with chain attached is used to lower it into a dissolver; the holder and chain are sacrificed during the dissolution process.

2.0 MECHANICAL PROCESSING OF FUEL IN SHIELDED DRY CAVES

During the past year (October 1958-October 1959) Oak Ridge National Laboratory has designed and fabricated much of the equipment necessary for investigating the feasibility of dejacketing metallic-clad NaK or Na-bonded fuels and the chopping and leaching of metallic-clad oxide fuels. Fuel types and the estimated dates at which mechanical processing may be attempted are:

<u>Fuel</u>	<u>Date</u>
<u>Dejacketing</u>	
Stainless steel clad, NaK or Na bond:	
SRE (Sodium Reactor Experiment)	1960, 1961
PRDC (Detroit Edison)	1962, 1963
CPPD (Consumers Public Power)	1964
<u>Chopping and Leaching</u>	
Stainless steel clad UO ₂ :	
Yankee Atomic ^a	1962
NMSR (Nuclear Ship Savannah)	1963
Stainless steel clad UO ₂ -ThO ₂ :	
Consolidated Edison	1964
Rural Cooperative Associates of Elk River	1964
Zircaloy-2-clad UO ₂ :	
FWR Blanket	1962

a. Not assigned to ORNL but might be available in small research and development amounts.

The purpose of evaluating mechanical processing techniques for these fuel types is to determine the economic feasibility of using mechanical head end treatment as a substitute for or in conjunction with chemical head end treatment. It is for these reasons, and because of the many unknowns involved in mechanically handling irradiated fuel, that these programs are purely of a research and development nature. It is conceivable, assuming that all experimental equipment gives outstanding performance, that the equipment now planned could handle as much as 190 kg of SRE fuel per day and 300 kg of chopped metallic-clad oxide fuel per day.

Equipment for the investigation of both mechanical head end steps will be installed in the ORNL High Level Segmenting Facility (HLSF) (Bldg. 3026). The dejacketing flowsheet will be investigated first, and then the equipment will be removed and the equipment for the chop-and-leach flowsheet installed.

The HLSF consists of two stainless steel-lined connecting shielded cells, A, 25 ft long by 10 ft wide by 15 ft high, and B, 15 ft long by 10 ft wide by 15 ft high, and one storage cell (painted) 21 ft long by 9.5 ft wide by 10 ft high with 5-ft thick normal concrete walls and bromine-filled windows. An underground tunnel located at right angles to the face of cell A, 47 ft long and equipped with tracks and a cart, connects cell A to the storage cell. Cell A is equipped with a General Mills Manipulator, a 3-ton crane and Model 8 manipulators; cell B with Model 8 manipulators only; and the storage cell with a 1-ton crane, Lee manipulator, and Model 8 manipulators.

During cell operation ~2 in. of water vacuum is maintained on all cells at an air throughput of ~1000 cu ft/min. Air leaving the cells is passed through absolute filters and then to the ORNL central off-gas facility. An internal air treatment system consisting of a cyclone, filters, and jet exhausting back to the cell is used to minimize the spread of particulate matter in the cell proper. If CO₂ or inert gases are being released in the cell to extinguish fires, the cell pressure is kept only very slightly subatmospheric. The fire-fighting equipment operates for 30 min releasing CO₂ at a rate of 2250 cu ft/min for the first minute and 450 cu ft/min for the next 29 min.

2.1 Dejacketing Head-End Step

Equipment designed specifically for dejacketing the fuel rods from the Sodium Reactor Experiment core 1 has been fabricated and is undergoing initial evaluation testing with prototype fuel. This equipment and the location of each component in Cell A are shown in Figs. 4, 5, and 6. The equipment in Cell A performs the following

Fig. 4—Proposed installation of SRE fuel element reprocessing equipment (Bldg. 3026, plan view, cell "A").

Fig. 5—Proposed installation of SRE fuel element reprocessing equipment (Bldg. 3026, front elevation, cell "A").

ELEVATION "B-B"

ELEVATION "C-C"

ELEVATION "D-D"

Fig. 6—Side elevations of SRE reprocessing equipment (Bldg. 3026).

stepwise mechanical handling operations: unloading of fuel, dismentling, dejacketing plus NaK and oil disposal, fuel washing and canning, and storage. The carrier is first transported to Cell A and the treated fuel is ultimately transported from the storage cell to the dissolver.

Detailed operating procedures and the time estimated for carrying out each step are presented in Sect. 3.1 and 3.2, respectively, and the anticipated maintenance problems in Sect. 3.3. A brief description of equipment and a summary of operational information developed for each step follow.

2.1 1 Carrier Transport

There are 55 fuel clusters to be processed from core 1 irradiations of the SRE. Each cluster (Fig. 7) consists of a circular bundle of seven fuel rods secured to spiders at each end and separated from each other by a spiral wire, 0.091 in. dia, wrapped around each rod except the center one. The seven rods (Fig. 8) contain 69 lb of natural uranium, each rod holding 12 natural uranium slugs 6 in. long. The first shipment of core 1 clusters will be made in November 1959 in a special 29-ton carrier (Fig. 9) secured to a railway flatcar. Each carrier accommodates 10 fuel storage cans and each can contains a single spent cluster. The cans are placed in an indexed rotatable poisoned rack (Fig. 10) to prevent a critical event. Once the carrier is brought into position against the charger door opening (Fig. 4), the cans are pushed one by one through an unloading port onto the traversing table (Fig. 11). The traversing table, which can travel the entire length of the cell; is equipped with holddown clamps for holding the fuel bundle during sawing of the end hardware to separate the bundle into individual rods

2.1.2 Disassembly and Particle Collection

End hardware is removed by a plunge cut of the multipurpose abrasion disk saw (Fig. 12 elevation C-C of Fig. 6). During cutting the SRE fuel cluster is contained in an enclosure and by means of a sliding seal (see Detail-Cutting and Particle Collection of Fig. 12). All particulate matter is trapped inside the box and blade guard and directed to a collection system by a stream of air.

The multipurpose saw, fabricated by Ty-Sa-Man Company, Knoxville, Tennessee, is designed to make a 28-in. traverse cut and is capable of a 35-in. vertical travel above the saw table. The saw can be swung through 90° to make longitudinal plunge cuts, during which the traverse table acts as a feeding mechanism. The maximum size saw blade for which the saw is designed is 24 in. dia. A 16-in.-dia blade will normally be used for the SRE work.

Fig. 7—SRE fuel cluster.

Fig. 8—SRE fuel element.

Fig. 9—SRE fuel element carrier.

Fig. 10—Section of SRE fuel element carrier.

Fig. 11—Traversing table.

Fig. 12—Multi-purpose hydraulic disassembly saw.

The saw is hydraulically powered by a 15-hp drive capable of imparting a saw spindle speed from 250 to 3600 rpm at essentially constant horsepower, which makes it possible to use diamond-toothed, abrasive, or friction wheel saw blades. The entire arm and carriage can be swung 90° to either the left or the right for storage or to accommodate the handling of extra long fuel elements in the cell. The over-all height of the saw pedestal is 9 ft. Traversing and raising drives are hydraulically operated. The drive and lock for swinging the saw out of the way are air-operated

Dry cutting tests with an abrasion disk saw showed that approximately 0.1 min actual cutting time is required to remove the end spider of an SRE cluster section at a replacement blade cost of only \$0.13 per cluster. At least 43% of the particles produced by abrasion disk sawing are 149 μ or less in size (Table 2). The least saw blade consumption occurs at a feed of 6-10 in./min when cutting 347 stainless steel (Table 3), but smoother cuts and less burrs were obtained at 25-30 in./min.

Saw produced particles, including those attrited from the blade itself, are withdrawn from the box enclosing the work by an air stream which passes through the cell internal-air cleanup system, consisting of a cyclone and an absolute filter.

2.1.3 Dejacketing

The SRE fuel rods are hydraulically dejacketed under a low-flash-point mineral oil*, one rod at a time, in a unique mechanical dejacketing device (Figs. 13 and 14). This equipment cuts an end from a fuel rod (Fig. 15), applies hydraulic pressure (mineral oil) inside the jacket (Figs. 16 and 17), expands the jacket, cuts off the remaining end and displaces the NaK and slugs by hydraulic pressure or by a jack screw, and rolls up the empty tubular jacket (Fig. 18). The products produced are shown in Fig. 19. Preliminary tests show that the diameter of the tubular jacket is expanded 0.002 in. by a mineral oil pressure of 1200 psig and that the machine performs basically as it should. Minor refinements and adjustments are indicated, however, to attain the desired proficiency for the hot cell work.

In the event that there are fuel rods greatly distorted or bent which do not respond to the hydraulic dejacketing technique, they are cut into short lengths (6 in.) and pushed through a simple auxiliary dejacketer (Fig. 20) containing cutting plows.

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* No. 6 white oil, viscosity 55 to 65 Saybolt Universal Seconds at 100°F, sp gravity 0.8174 at 100°F; flash point, minimum 313°F (Mineral Refining Company)

Table 2. Particles Produced in Dry Abrasive-disk Cutting of
1/2-in.-o.d. Type 347 Stainless Steel Rods

U.S. Standard Sieve Screen Size, μ	Amount, wt %
< 149	43.0
149-177	9.8
177-210	0.8
210-250	8.7
250-297	2.9
297-420	10.9
420-590	8.0
590-840	10.7
840-2000	3.6
> 2000	1.6

Table 3. Abrasive Blade Consumption vs Feed Rate Conditions

Dry cutting with Raybestos Manhattan No. 239 blade,
16-in. o.d. x 1/8-in. thick, 2.7 g/cu cm (cost \$6.00 each).

Saw operated at 10,450 sfpm (surface feet/minute).

Type 347 stainless steel removed per cut was 1.15 cu cm
(9.2 g).

Feed Rate, in/min	Blade Consumed Per Cut		Part of Metal Removed Per Part of Blade Consumed	
	cu cm	g	By volume	By weight
6	0.27	0.74	4.26	12.4
10	0.28	0.77	4.11	11.9
15	0.31	0.85	3.71	10.8
20	0.34	0.92	3.39	10.0
25	0.37	1.0	3.11	9.2
30	0.40	1.07	2.88	8.6
35	0.43	1.15	2.68	8.0
40	0.45	1.2	2.56	7.7
45	0.48	1.3	2.40	7.1

Fig. 13—Hydraulic dejacketing equipment for SRE fuel rods.

Fig. 14—Prototype hydraulic dejacketing equipment for SRE fuel rods.

Fig. 15—Removal of ends from an SRE fuel rod by rotary cutters. (Support rolls are rotated while rotary cutters cut through cladding only. Inert ends are removed.)

Fig. 16—Expansion of SRE fuel rod jacket. (Hydraulic pusher propels fuel element into external collet. Kerosene at 800–3000 psi can be used to inflate the cladding. With the internal collet removed, the slugs may be flushed out with kerosene or ejected with the tubular jack screw into the basket receiver provided.)

Fig. 17—Hydraulic collet. (Jack screw with fuel rod on roll drive.)

Fig. 18—Rolling up of empty jacket. (One end of the empty cladding is flattened by GM manipulator and placed into the slot of a rotating reel. As the reel revolves, the cladding is formed into a flat spiral package approximately 3 in. in diameter.)

Fig. 19—Products of the hydraulic de-jacketing operation.

Fig. 20—Auxiliary SRE dejacketing die.

NaK and Oil Disposal. The NaK (22% Na, 78% K), approximately 98 ml/rod, discharged from each dejacketing operation is drained from the bottom of the hydraulic dejacketer collection trough and reacted with steam in a nitrogen-blanketed NaK reactor. Steam supplied at a rate not to exceed 3 ml of water per minute reacts with NaK under oil, without flashing or burning, liberating hydrogen at 1.8 liters/min (Fig. 21).

Oil is disposed of by simply flushing it through the reactor in the presence of steam and discharging it to a "hot" waste line.

2.1.4 Fuel Washing and Recanning

Slugs discharged into mineral oil from the dejacketing operation require cleaning to remove residual NaK clinging to its surface and to remove the mineral oil, which might contaminate the subsequent chemical processing steps. A slug washer (Figs. 22 and 23), operated with steam at 45 psig at approximately 3 lbs of steam per minute, rotates a basket of slugs at approximately 1000 rpm by impingement of the steam against the basket. The steam reacts with the NaK and removes the oil. A cleaning time of at least 10 min is required.

Steam-cleaned slugs from one rod are canned in an aluminum can with a simple commercial* canning device (Fig. 24). The amount of aluminum required to can the uranium is 1.3% of the weight of uranium canned. A typical can weighs 132 g. Recanning of the washed slugs is to facilitate their handling at ORNL and it is not a normal requirement.

2.1.5 Storage and Transport to a Dissolver

Canned slugs are placed seven cans to a storage crate and are transported underground on a cart from Cell A to the storage cell (Fig. 25). Crates are stacked in tiers of three, one-half of the core on each side of the cell. This array is critically safe even if moderated with natural water.

Fuel is withdrawn from the storage cell via a charger cask (Item 7 of Fig. 25), which holds seven cans atop each other. The charger cask is placed vertically on the slug chute leading to a water-filled dissolver, and disgorges the seven cans by gravity in a single event.

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* Max Ams Machine Company, Bridgeport, Connecticut.

Fig. 21—Hydrogen evolved from a NaK-steam reaction.

Fig. 22—SRE slug washer installation.

Fig. 23—SRE slug washer on test stand.

Fig. 24—SRE slug canning operation.

Fig. 25—Storage cell Bldg. 3026.

2.2 Shearing (Chopping) and Leaching Head-end Step

The successful removal of inert end adapters and other hardware from spent metallic-clad oxide fuel and the subsequent shearing (chopping) and leaching of entire fuel assemblies should result in a decreased amount of inert metal to be processed with the fissile and fertile metal, increasing the capacity of a processing plant and decreasing the quantity of aqueous waste discharged. Processing of fuel with nitric acid-insoluble jackets by existing processing plants in conventional stainless steel equipment should also be possible. Oak Ridge National Laboratory is seeking to establish the economic feasibility of a mechanical-disassembly chopping-and-leaching head-end step. Information developed on a research and development level thus far for such a mechanical head end step follows.

2.2.1 Disassembly

The removal of inert end hardware from the fuel types listed in Table 1 by dry abrasive disk sawing appears to be feasible. Replacement blade cost and the amount of waste produced in removing inert end adapters from typical reactor fuel assemblies were computed for the Ty-Sa-Man hydraulic saw cutting with a 16-in. dia Manhattan No. 239 abrasive blade. Calculations based on the cutting rates shown in Table 3 show that the cost of the abrasive blades consumed would range from \$0.13 to \$1.19 per assembly and that the total volume of waste produced will be from 16.6 to 184 cu cm or 119 to 1252 g per assembly (Table 4). The actual cutting time (not including set-up time) varies from 0.1 to 1.0 min based on a feed rate of 30 in./min. This feed rate produced satisfactory cutting at a wear ratio, by volume, of 1 part of blade consumed to 3.5 parts of metal removed.

The relatively high cost indicated for cutting a Consolidated Edison assembly is the result of a large cross section and the number of cuts required, which necessitate frequent blade changes if the cross section is to be completely severed by two cuts. Actually, the used blades are only slightly consumed and if salvaged and re-used for cutting fuels of smaller cross section would result in a marked decrease in cutting cost.

Longitudinal cutting of tube bundles at the ferrules separating rows of tubes is not feasible with thin, 1/8-in.-thick, abrasive disks because of blade breakage. However, thin blades made of metal have not been evaluated.

Separation of tubular assemblies into smaller sections of tube sheets by impact wedge breaking of metallic bond at ferrules appears feasible if a brittle braze material such as Nicrobraz-50 is used in fabrication (Figs. 26 and 27).

Table 4. Disassembly of Stainless Steel Fuel Assemblies by Dry Abrasive Sawing

Abrasive: Manhattan No. 239 blade, 16 in. dia x 1/8 in. thick; cost \$6.00 each

Operating speed: 10,450 sfpm

Feed rate: 30 in./min

Wear ratio: 1/3.5 (parts abrasive consumed/metal removed)

	Reactor				
	Consolidated Edison	Nuclear Ship Savannah	Rural Coop	Yankee Atomic	SRE
Assembly cross section, in.	5.755 sq	8.9 sq	3.87 sq	7.66 sq	2.79 dia
Material	S.S.	S.S.	S.S.	S.S.	S.S.
Number of rods to cut	824	42	50	50	7
Rod o.d., in.	0.3	0.6	0.45	0.4	0.375
Depth of cut, in.	2.86 ^b	4.5 ^b	3.87 ^c	3.83 ^b	2.79 ^c
Usable blade radius, in.	2.26	0.625	1.25	1.3	2.33
Metal waste, cu cm	143	24.4	16.3	12.9	15.8
g	1142	196	130.4	107	127
Abrasive waste, cu cm	41	8.15	4.66	3.7	4.53
g	110	18.9	12.6	11.6	12.2
Total waste, cu cm	184	32.55	20.96	16.6	20.4
g	1252	217	143	118.6	139
Number of assemblies cut per blade consumed	5	5.5	27.2	38.3	46.6
Cutting time, ^d min	1.0	0.6	0.26	0.51	0.1
Number of cross-sectional cuts	6	2	2	2	1
Abrasive blade cost, \$/assembly	1.19	1.09	0.22	0.16	0.13

^a Assuming Zircaloy-2 is cut at the same rate as stainless steel.

^b Assembly rotated for 2 cuts.

^c Cut complete in one pass.

^d Cutting time only; set-up time not included.

Fig. 26—Wedge splitting of a microbrazed assembly.

Fig. 27—Portions of tube bundle produced by wedge splitting.

It is not possible to disassemble a simulated Consolidated Edison prototype fuel assembled with Coast Metals 50 brazing metal, using the same impact wedge which successfully disassembled a similar unit brazed with Nicrobraz 50, because of the greater ductility of this type of braze material. The composition of the two brazing metals are

<u>Nicrobraz 50</u>		<u>Coast Metals 50</u>	
Nickel	74%	Nickel	93.2%
Phosphorus	10% $\pm$ 1%	Silicon	3.5%
Chromium	13% $\pm$ 2%	Boron	1.9%
		Iron	1.4%

It is the embrittling quality of the 10% phosphorus in Nicrobraz which makes disassembly easy. The Coast Metals braze will probably not be considered for use in fuel elements because of the high neutron absorption cross section of the boron constituent. However, application of this technique to ductile braze joints is being further investigated in anticipation of their possible future use.

2.2.2 Shearing Studies

The feasibility of shearing tubular fuel bundles has been investigated in tests performed by Oak Ridge National Laboratory and through subcontracts to Clearing Machine Co., Chicago, Illinois, and Birdsboro Machine and Foundry, Birdsboro, Pennsylvania. A Mark I prototype fuel bundle (Fig. 28) or single stainless steel tubes filled with porcelain or UO₂ pellets were sheared to determine blade shape, life, clearance, velocity, hardness, and satisfactory alloy; thrust requirements; dislodgment of ceramic core and the production of metallic fines; design criteria for a prototype shear; and collection method for sheared product. Shearing of the spent fuel assemblies is indicated to be feasible from information obtained from these test programs. However, this cannot be definitely established until more definitive data are obtained in two areas of development: (a) A reasonably low rate of blade wear and galling must be demonstrated in the presence of hard Nicrobraz over several thousand cuts; and (b) an experimental procedure must be demonstrated for shearing the last piece of a fuel bundle into 2-in. maximum length pieces, or these rigid requirements must, if possible, be relaxed.

Blade Shape. Blade types evaluated at Clearing, Birdsboro, and ORNL are shown in Figs. 29, 30, and 31, respectively. In the Birdsboro and ORNL tests a Mark I was sheared in the "as is" condition, but a deferruled version, rearranged (Fig. 32) was used in the idealized Clearing test. Test data are reported in **Tables 5-7.**

A stepped punch (blade)(Fig. 31) working against a circular or V-shaped anvil is superior to the other combinations tested because it produces maximum breakage of core, requires lower tonnage, and gives the

Fig. 28—Prototype fuel element Mark I.

Fig. 29—Shear blade configurations-clearing shear blade tests.

PUNCH							
ANVIL							
LEGEND	A	B	C	D	E	F	G

COMBINATIONS USED:

A-B

E-F

A-F

C-D

G-B

Fig. 30—Shear blade combinations used in shear blade evaluation program at Birdsboro.

Fig. 31—Various interchangeable punches and anvils for use in mechanical processing blade evaluation studies at ORNL.

Fig. 32—Clearing shear blade tests-fuel element tube holder.

Table 5. Size Distribution of Porcelain and Metal Fines from Shearing of Mark I Prototype Fuel Assembly in Clearing Shear Blade Evaluation Program

Conditions Shear - 300 ton hydraulic press for 0.5-in./sec blade velocity, 110 ton OBI mechanical press for 48 in./sec blade velocity

Blade type - "plane of contact" blades

Tests - 10 to 25 cuts of a 36 tube highly constrained bundle with no ferrules (0.5-in. 30 mil wall S.S. 304L tubing, porcelain filled)

Physical characteristics of porcelain - Tensile strength, 5-10,000 psi, compressive strength, 90,000 psi, flexural strength, 10-20,000 psi, hardness, 77-9 moh scale

Blade				Metal and Porcelain										Metal						
Combination	Velocity (in./sec)	Sharp or Dull	Clearance Between Blades (mils)	Maximum Shearing Force (tons)	Percent of Total Sheared Product ¹	Percent Fines Appearing in Various Size Ranges						Porcelain Percent of Total	Percent of Total	Percent Metal of Various Size Ranges						
						Over 1680 Microns	1680 to 840 Microns	840 to 297 Microns	297 to 149 Microns	149 to 74 Microns	Under 74 Microns			Over 1680 Microns	1680 to 840 Microns	840 to 297 Microns	297 to 149 Microns	149 to 74 Microns	Under 74 Microns	
	A	0.5	S	1	43	4.25	5.90	8.04	33.30	18.70	12.70	21.20	98.44	1.56	18.39	4.80	0.59	0.16	0.03	0.11
	A	0.5	S	3	39	3.94	6.89	18.59	31.18	18.14	10.94	14.24	98.30	1.70	6.96	4.99	0.78	0.17	0.17	0.17
	A	0.5	S	10	40	5.08	5.00	18.85	32.00	17.70	9.75	16.80	97.78	1.22	5.31	3.89	0.48	0.11	0.15	0.19
	A	0.5	D	1	40	5.46	7.14	13.85	29.10	17.00	11.10	21.80	97.82	2.18	16.90	5.03	0.66	0.16	0.14	0.24
	A	0.5	D	10	51	6.30	6.52	13.33	31.30	17.40	11.40	21.00	98.49	1.51	13.43	4.01	0.66	0.10	0.13	0.24
	A	48	S	1	-	6.00	8.2	16.60	29.60	17.90	10.95	16.60	98.96	1.04	7.81	4.88	0.28	0.31	0.29	0.38
	A	48	S	5	-	6.82	5.72	17.00	31.10	18.00	11.00	17.10	98.26	1.74	13.10	3.86	0.45	0.21	0.22	0.29
	B	0.5	S	1	30	3.37	10.25	23.60	32.30	15.07	8.72	10.03	97.65	2.35	5.19	5.02	1.04	0.27	-	0.21
	B	0.5	S	5	30	2.95	10.10	22.65	33.20	14.65	8.32	11.50	98.27	1.73	3.48	4.13	0.92	0.32	0.35	0.46
	B	0.5	S	10	34	4.32	10.29	20.13	32.55	15.32	9.50	12.19	98.24	1.76	3.67	5.11	0.78	0.26	0.31	0.32
	B	0.5	D	1	37	4.43	12.70	21.90	30.60	14.40	8.90	11.50	98.61	1.39	4.15	2.81	0.54	0.21	0.22	0.23
	B	0.5	D	5	38	3.86	7.04	21.10	32.55	16.13	9.66	13.52	98.02	1.98	6.01	4.72	0.64	0.27	0.24	0.33
	B	0.5	D	10	39	3.86	5.66	19.37	32.70	16.80	10.50	15.07	98.60	1.40	7.90	3.32	0.57	0.28	0.28	0.37
	B	48	D	1	-	4.02	10.63	23.85	33.80	14.62	8.50	8.50	98.23	1.77	8.33	3.20	0.68	0.64	0.96	1.23
	B	48	D	5	-	4.72	9.74	24.65	33.90	14.90	8.64	8.16	96.39	3.61	5.84	2.21	6.83	0.43	0.53	1.23
	B	48	D	10	-	5.27	9.30	25.80	33.70	13.80	7.84	9.52	98.12	1.88	5.53	1.92	0.87	0.40	0.39	0.64
	B	48	S	1	-	6.27	7.41	16.10	28.90	14.50	8.47	24.30	98.82	1.18	7.14	2.70	0.46	0.31	0.29	0.37
	B	48	D	5	-	4.72	9.74	24.65	33.90	14.90	8.64	8.16	96.39	3.61	5.84	2.21	6.83	0.43	0.53	1.23
	C	0.5	S	1	28	4.91	4.27	15.80	29.90	17.95	12.00	20.10	98.20	1.80	13.16	5.77	0.62	0.25	0.02	0.06
	C	0.5	S	5	33	5.48	14.00	18.87	27.65	14.80	9.48	15.45	98.91	1.09	2.75	2.52	0.56	0.14	0.16	0.26
	C	0.5	D	6	34	6.50	10.95	17.37	26.92	14.98	10.10	19.67	98.64	1.36	3.67	4.59	0.29	0.15	0.17	0.20
	D	0.5	S	1	45	4.65	4.35	15.60	30.50	15.70	12.20	21.80	98.85	1.15	8.54	6.19	0.72	0.20	0.17	0.26
	D	0.5	S	5	45	6.00	4.95	15.40	31.40	19.40	6.40	22.90	96.86	3.14	11.87	4.54	0.58	0.24	0.21	0.45
	D	0.5	S	10	43	5.86	4.70	16.70	34.50	20.60	13.50	9.95	98.07	1.93	15.64	5.49	0.58	0.19	0.17	0.31
	D	0.5	D	1	45	7.70	7.67	15.60	29.30	17.9	10.40	19.40	97.96	2.04	16.18	4.47	0.62	0.20	0.28	0.35
	D	0.5	D	10	46	6.96	4.41	14.92	30.1	17.8	11.35	31.38	98.71	1.29	6.94	3.87	0.59	0.16	0.15	0.23
Average						5.16							98.25	1.75						

¹ Divided by 0.437 $\left(\frac{\text{wt porcelain}}{\text{wt porcelain} + \text{wt steel}} \right)$ to obtain "Percent of Porcelain dislodged."

Table 6. Size Distribution of Porcelain Fines from Shearing of Mark I Prototype Porcelain Filled Tubular Assembly in Birdsboro Shear Blade Evaluation Program

Conditions

- A Shear - 100 ton open throat hydraulic driven straightening press driving self contained die set
 B Blade type - initially sharp 'plane of contact' blades
 C Five cuts at 1.0 in. lengths of a Mark I porcelain filled assembly at each set of experimental conditions
 D Physical properties of porcelain
     Tensile strength 5-10,000 psi
     Compressive strength 90,000 psi
     Flexural strength 10-20,000 psi
     Hardness 7-9 mohr scale
     Squarekeen #3
 E Blade material

Blade Shape	Velocity (in./sec)	Maximum Shearing Force		Clearance Between Blades (mils)	Porcelain ¹ Percent	Percent of Total Porcelain in Various Size Ranges ²							
		At Ferrules (tons)	Not at Ferrules (tons)			Over 1680 Microns	1680 to 840 Microns	840 to 297 Microns	297 to 149 Microns	297 to 100 Microns	149 to 74 Microns	Under 100 Microns	Under 74 Microns
	2	84	74	3	5.4	10.0	7.8	45.7		6.8		29.7	
	2	84	67	10	12.0	5.6	17.9	31.4		15.9		29.2	
	2			22	13.9	8.8	21.5	33.7		14.5		21.5	
	12	84	74	3	17.5	7.5	20.5	33.9		14.8		23.3	
	12	84	74	10	9.3	7.7	22.7	34.7		15.0		19.9	
	12	100		22	11.9	10.9	24.0	34.7		14.9		15.5	
	36	84	74	3	7.8	8.9	7.8	41.1		17.9		24.3	
	36	84	67	10	8.7	7.0	20.5	33.1		15.5		23.9	
	2	73	67	4	11.5	9.1	21.7	34.5		16.3		18.4	
	2	80	70	11	7.7	7.1	20.6	36.2		16.4		19.7	
	2	100	70	21	9.0	4.6	20.4	35.6		16.7		22.7	
	12	77	74	4	8.3	8.6	22.4	34.9		15.5		18.6	
	12	80	77	11	8.4	7.2	20.5	34.1		15.3		22.9	
	12	80	77	21	10.3	9.1	21.3	32.2		15.1		22.3	
	36	84		4	8.6	7.1	21.6	34.8		16.0		20.5	
	36	84		11	7.1	6.8	20.1	37.6		16.7		18.8	
	36	84		21	7.5	7.0	22.1	36.7		16.0		18.2	
	2	53	44	3	7.2	14.8	20.6	32.8		15.1		16.7	
	2	57	50	10	10.53	7.70	18.37	31.60	15.58		9.90		16.90
	2	60	50	20	10.67	7.36	17.8	31.01	15.73		9.90		18.23
	12	70	54	3	9.6	6.9	21.4	33.7		15.5		22.5	
	12	60	54	10	10.5	9.07	18.52	31.1	15.6		9.76		16.0
	12	57	53	20	12.42	15.21	16.22	31.90	17.0		10.85		18.83
	36	73	53	10	10.35	7.15	18.84	31.25	15.77		9.9		17.10
	36	53	50	20	8.87	7.81	17.52	31.16	16.00		10.0		17.52
	2	73	57	4	11.59	7.53	18.81	33.73	16.09		9.74		14.1
	2	94	57	11	10.15	7.05	17.75	33.62	15.85		9.42		15.31
	2	84	70	20	6.93	4.54	14.86	32.50	17.7		11.84		18.87
	12	80	74	4	8.05	9.83	21.00	33.85	14.50		8.68		12.18
	12	77	70	11	6.62	6.72	19.03	33.67	15.97		9.84		14.08
	12	77	70	20	8.44	7.44	19.20	33.45	19.70		9.40		14.93
	36		67	4	8.06	11.20	21.23	32.55	14.34		8.59		12.1
	36			11	5.91	4.89	17.45	34.26	16.23		10.5		16.67
	36			20	6.29	7.0	18.40	34.02	16.66		10.04		13.9
	2	77	50	4	11.1	7.93	19.06	33.94	16.26		9.7		13.11
	2	77	64	10	9.34	6.89	18.29	33.56	16.26		10.19		14.81
	2	80	77	22	9.08	8.80	19.72	32.96	15.6		9.52		13.45
	12	84	77	4	8.8	9.14	18.98	33.07	15.42		9.62		13.77
	12	77	67	10	8.0	9.32	21.17	33.39	15.38		9.16		11.60
	12	90	77	22	10.61	6.18	19.40	34.0	16.00		9.7		15.0
	36			4	8.26	5.88	19.08	33.83	16.14		9.65		15.1
	36	84		10	9.37	9.92	22.50	34.0	15.24		8.62		9.74
	36	84	74	22	9.04	7.2	19.3	33.19	16.26		9.89		14.18
Average					9.83								

¹Divide cuts by 0.437 to obtain "Percent of Porcelain" dislodged

²A correction for those metal fines included in sizes less than 840 micron was not made. Previous information indicated this would be a negligible quantity and Fe analyses were not made

Table 7. Size Distribution of Porcelain Fines from Shearing of Mark I Prototype Porcelain Filled Tubular Assembly in ORNL Shear Blade Evaluation Program

Conditions: a) Shear - self contained die set installed in 150 ton vertical operating clearing press

b) Blade type - initially dulled¹

c) 10 - 1.0-in. length cuts with each blade shape combination of anvil and punch. Blade velocity ~2 in./sec. Clearance between blades 0.003-in.

d) Shear blade material: Carpenters Vega, shear blade hardness: 56-57 Rockwell C

e) Physical properties of porcelain: Tensile strength 5-10,000 psi
Compressive strength 90,000 psi
Flexural strength 10-20,000 psi
Hardness 7-9 moh scale

Blade Shape	Combination	Shearing Force (tons)		Percent ³ of Total Sheared Product	Porcelain ² Percent in Various Size Ranges					
		At Ferrules	Not at Ferrules		Over 1680 Microns	1680 to 840 Microns	840 to 297 Microns	297 to 149 Microns	149 to 74 Microns	Below 74 Microns
	P12 D8	75	50	9.68	3.51	19.33	31.14	16.87	10.14	19.01
	P14 D6	-	70	6.25	7.27	18.46	33.36	15.77	9.62	15.52
	CP9 D5	90	75	6.53	7.65	19.99	33.29	15.06	9.07	14.95
	P14 D8	85	75	6.30	8.45	20.39	32.52	14.72	8.82	15.09
	CP9 D8	-	75	8.22	6.48	17.69	31.10	14.93	9.02	20.79
	P9 D6	85	-	5.53	6.75	18.36	32.73	15.46	9.87	16.84
	P10 D6	100	80	4.46	7.70	20.63	32.24	14.86	8.98	15.60
	P10 D5	-	70	7.20	6.95	19.91	32.66	15.53	9.29	15.66
	P9 D5	90	75	6.93	7.34	20.62	32.36	15.22	9.19	15.30
	P13 D5	100	70	7.07	7.60	20.40	32.79	15.24	9.04	14.92
	P14 D5	-	-	6.17	6.00	18.83	33.50	16.59	9.92	15.20
	P11 D5	-	70	6.85	8.70	19.66	31.62	14.14	9.44	16.50
	CP9 D6	90	75	5.58	6.25	19.01	32.19	15.84	9.65	16.97
	P9 D8	-	75	6.11	6.64	18.17	32.04	16.00	9.82	17.33
	P13 D6	100	80	5.52	7.78	19.12	32.10	15.13	9.50	16.40
	P11 D6	110	70	6.01	6.20	18.22	32.05	15.74	10.00	17.80
	P12 D6	60	45	8.51	7.20	18.70	32.00	15.67	9.51	16.90
	P13 D8	95	80	5.96	6.70	19.10	32.30	15.39	9.76	16.82
	P10 D8	95	75	6.93	5.70	18.32	33.10	16.00	9.75	17.20
	P12 D5	-	55	8.87	9.50	20.12	31.72	15.11	8.90	14.70
Average				6.73						16.0

¹By grinding 1/32-in. radius on blade edge.

²A correction for those metal fines included in sizes less than 840 microns size was not made. Previous information indicated this would be a negligible quantity and Fe analyses were not obtained.

³Divide by 0.437 to obtain "Percent of porcelain" dislodged.

best separation at ferrule locations. It required approximately 40% less shearing thrust at nonferrule location shearing with 45 tons vs the 75-ton requirement for the other blades. This punch in combination with either the D-8 or D-3 anvil is considered the best blade shape tried (Tables 5-7). It is recommended primarily because of its superior performance in producing discrete single pieces and more fines in combination with any anvil than any other punch. There were 22 and 20% dislodgment of the available porcelain, respectively, in combination with the D-8 and D-5 anvils and an average dislodgment of 15% of all ORNL blade combinations (Table 7).

Blade Life. The life of a shear blade is probably long, although the scope of these tests did not permit a conclusive demonstration of shear blade life. Blade life is estimated to be 10,000 - 50,000 cuts. Assuming a blade life of 4,500 cuts and a blade assembly cost of \$1000 each, the unit cost for expendable blades for shearing the spent reactor fuels of consideration in this program was negligible and varied from 1.28×10^{-3} to 23.1×10^{-3} mil per kilowatt of power produced. This cost is probably conservative since cuts into longer pieces (2-3 in.) may prove to be optimum for the batch leaching of UO_2 cores.

A longer blade life may be expected in the slower range of speeds from 1 to 5 in./sec than at higher speeds of 48 in./sec with essentially no change in appearance of the sheared pieces. It appears desirable to start shearing, and maintain, insofar as possible, a clearance between blades of 3 mils so that a maximum number of cuts may be made before excessive wiping of metal between the blades finally occurs at approximately 22 mils' clearance. (Wiping may occur at less than 0.022 in. for tubes less than the 35-mil wall thickness of the Mark I.) It may or may not be possible to shear the Zircaloy-2-clad fuels listed in Table 1 and Sect. 2.0 because of hazards associated with the metal fines produced by shearing.

Blade Clearance. Oak Ridge National Laboratory tests showed that a blade clearance of 1-3 mils is desired; otherwise thin pieces of Microbraz-50 create a major galling and chipping problem. Clearing's test findings were similar and Birdsboro's tests showed that a clearance as great as 10 mils was not unreasonable.

The initial blade wear which occurs by chipping appears to be eliminated without affecting the quality of the sheared product by grinding a 1/32-in. radius on the blade edge.

Blade Velocity. A practical maximum limitation of blade velocity was determined for shearing the Mark I prototype assembly in Clearing's tests. At 48 in./sec blade velocity there was excessive blade wear after six cuts from galling between blades by metal particles. Particles became welded during the impact of the top blade at the highest shearing velocities. In the Clearing tests on shearing of unferruled assemblies,

the severity of galling was indicated by the accompanying substantial increase of shear thrust, from 35-47 tons of more than 110 tons, required for shearing the bundle. Blade velocities of 1-2 in./sec minimize the hydraulic system required and produce an acceptable product.

Blade Hardness and Alloy. It is not clear at this time what the blade hardness should be and the type of alloy. Consultation suggests Rockwell C-59 for hardness and dissimilar alloys of Carpenter steel for blades and guides. Since the components of the shear should be nitric acid resistant, the final decision awaits the results of a test program combining wear and chemical resistance evaluations.

Thrust Requirements. A minimum thrust of 270 tons is required to shear the six assemblies considered in this program if the Nuclear Ship Savannah fuel is reduced to subassemblies (**Table 8**). This thrust was calculated from an experimental average measurement of 80 tons required to shear a Mark I prototype fuel assembly. The separate contributions of metal and porcelain to the total thrust requirement for shearing were calculated from the revised Hanford shear data in which the S_c (critical shear strength) for porcelain (or UO_2) was 9000 psi and for 304L stainless steel was 57,000 psi. The calculated total thrust checked the experimentally determined 80 tons within the limits of experimental accuracy. A thrust of 367 tons required for the Nuclear Ship Savannah assembly is the maximum requirement if no disassembly is made.

A 3% increase of power requirement was observed in Clearing's tests after increasing the clearance from 1 to 10 mils between the inverted V punch and anvil. The shear power requirement increased 25% when the inverted V blade edge was artificially dulled by grinding to a 1/32-in. radius, but the quality of cutting was not noticeably affected. The Clearing tests show that when a blade is dulled an increase in thrust is required to do the same shearing job. For example, after 300 cuts were made on a Mark I with the inverted V blade, the thrust requirement increased 7%. There was no measurable increase in clearance between blades after 300 cuts.

The thrust requirement for shearing the Mark I at ferrule locations was unpredictable and in some cases was 80% higher than the force required to shear at a nonferrule section under the same operating conditions. For example, the CP8-D6 blades required 80 and 145 tons to shear at these different locations. This unpredictable high thrust requirement at some of the ferrule sections will be anticipated by installing a sensing device which will not permit the bundle to advance until the cross section is completely severed, using as many chops on the same spot as are necessary.

Dislodgment of Ceramic Core and Stainless Steel Fines. The average amounts of porcelain dislodged from shearing a Mark I prototype filled with porcelain into 1-in. lengths in the Clearing, Birdsboro, and ORNL

**Table 8. Thrust Requirements for Shearing Fuel Assemblies
of Interest in the Mechanical Processing Program**

Basis: one fuel assembly

Fuel Type	Basis for Thrust Calculations				Total Shearing Thrust, tons	
	304 Stainless Steel		Ceramic			
	(a) Shearing Thrust	Requirement, tons (Sc = 57,000 psi)	(b) Shearing Thrust	Requirement, tons (Sc = 9,000 psi)	(a) + (b)* Calculated	Experi- mental
	Cross Section, sq in.		Cross Section, sq in.			
Mark I Prototype	1.835	52.3	5.22	23.5	76	80**
Nuclear Ship Savannah	9.27	264	22.9	103	367	-
Yankee	6.27	179	20.25	91	270	-
PWR blanket I	3.86	110	12.05	54.2	164	-
Consolidated Edison	3.72	106	11.28	50.8	157	-
Rural Coop	0.675	19.25	3.25	14.62	34	-

*Considering only the metal in tube walls and the ceramic and neglecting cross section of ferrules and straps.

**The same total shearing thrust was required within the limits of experimental error at a ferrule as a nonferrule cross section

tests were 11.9, 22.6 and 15.4%, respectively (**Tables 5-7**). Ceramic dislodgment was minimum in the Clearing tests with a blade clearance of 5 mils and bundle orientation that gives maximum support to the individual tubes of a bundle (**Table 9**). For the three test programs, approximately 85% of the porcelain dislodged was 1700 μ or less and from 12 to 28% was 100 μ or less (Figs. 33 and 34).

It is estimated that a stepped blade shearing UO₂ into 1-in. lengths under similar conditions as for porcelain would dislodge approximately 50% of the UO₂ present. This estimate was made by taking the amount of fines produced by a stepped blade from **Table 7** and multiplying it by a factor of 2.1. The factor of 2.1 was obtained by shearing single tubes of stainless steel filled with porcelain and comparing the amount dislodged with the amount of UO₂ dislodged, as shown in Fig. 35. Five per cent of this UO₂ dislodged would be less than 1- μ size (Fig. 36).

The effect of varying length of cut on UO₂ dislodgment from single 0.4-in.-dia stainless steel-clad UO₂ rods sheared with a "line of contact" blade may also be observed from Fig. 35. The percentage of UO₂ separated from 15 cuts of each specified sheared length varied from 30% for 0.5-in. sheared lengths to 2% for 5-in. lengths when single 0.4-in.-dia stainless steel-clad UO₂ were sheared with a 60-ton "line of contact" blade. The percentage of UO₂ separated may be expressed as a function of the length in inches of sheared piece, L, by the equation

$$P = 13L^{-1.2}$$

The percentage of dislodgment of porcelain falls very close to the curve in Fig. 35 for 3/4- and 1-in. lengths of pieces sheared from a Mark I type porcelain-filled bundle with the 125-ton Manco shear using "plane of contact" blades. (Dislodgment for 3/4- and 1-in. lengths are 27 and 12% in shearing a Mark I assembly with the 125-ton Manco.) The variation of dislodgment of UO₂ with length of cut in shearing a UO₂-filled bundle is not known.

In separate tests with the 125-ton Manco shear with plane of contact blades on a Mark I prototype, the percentage of particles of a given size range is greater for the shorter lengths than for the longer (Fig. 36).

Stainless Steel Fines

The minimum production of stainless steel fines from tubular assemblies may be expected under conditions where minimum plastic deformation of stainless steel clad is permitted as in Clearing's tests of **Table 5**. There was an average of 1.75% metal fines appearing in the total metal and porcelain fines in comparison with 0.7% from shearing the ferruled Mark I porcelain-filled bundle in earlier tests (**Table 10**) with the 125-ton Manco shear using a specific "plane of

Table 9. Effect on Porcelain Dislodgment of Operating Variables
(Clearing's Tests)

Shearing of a highly constrained bundle of 36 stainless steel-clad porcelain tubes

Shears: self-contained die set driven by 300-ton hydraulic press for low-velocity tests and 110-ton open back inclinable press for high-velocity tests

Tests: 25 tests involving four blade combinations

Clearance between blades: 0.001-0.010 in.

Blade velocity: 0.48-48 in./sec

Blade type: "plane of contact"

Operating Conditions	(a)	(b)	(c)	(d)
0.48 in./sec, sharp blade				
Clearance, mils	1 → 5 → 10	1 → 5 → 10	1.0 → 5	1 → 5 → 10
Porcelain* production, %	4.2 → 3.9 → 5.1	3.4 → 3.0 → 4.3	4.9 → 5.5	4.7 → 6.0 → 5.9
0.48 in./sec, dull blades				
Clearance, mils	1 → 10	1 → 5 → 10	-	1 → 10
Porcelain* production, %	5.5 → 6.3	4.4 → 3.9 → 3.9	-	7.7 → 7.0
0.48 in./sec, sharp blade				
Clearance, mils	1 → 5	1	-	-
Porcelain* production, %	6.0 → 6.8	6.3	-	-
0.48 48.0 in./sec, sharp blade				
Clearance, mils	1	1	-	-
Porcelain* production, %	4.25 → 6.0	3.4 → 6.3	-	-
0.48 48.0 in./sec, dull blade				
Clearance, mils	-	1	-	-
Porcelain* production, %	-	4.4 → 4.2	-	-
Clearance, mils	-	5	-	-
Porcelain* production, %	-	3.9 → 4.7	-	-
Clearance, mils	-	10	-	-
Porcelain* production, %	-	3.9 → 5.3	-	-

*This includes a negligibly small percentage of metal fines.

Note: Data is not available for high velocity shearing with dull blades.

Fig. 33—Comparison of distribution of sizes of sheared procelain produced with different blade shapes ("plane of contact") under various noncomparable experimental conditions of shearing a Mark 1 procelain-filled fuel assembly prototype (deferruled for clearing tests) in three separate shear blade test programs.

Fig. 34—Comparison of distribution of sizes of sheared porcelain produced with different blade shapes under comparable experimental conditions of shearing a Mark 1 porcelain-filled fuel assembly prototype in the Birdsboro and ORNL shear blade test programs.

Fig. 35—Percent of UO_2 separated from single 0.4-in.-dia stainless steel clad UO_2 rods vs. length of sheared piece. ● Stepped blade; x Plane-of-contact blade.

Fig. 36—UO₂ and porcelain size distribution from shearing metal clad ceramic filled tubes.

Table 10. Size and Weight Distribution of Porcelain and Metal Fines from Shearing of Mark I Prototype Fuel Assembly

Shear: 125-ton Manco
 Blade type: "plane of contact"
 65 cuts at 0.75-in. lengths of a 4-ft
 Mark I prototype at 0.33 in /sec
 Physical properties of porcelain:
 Tensile strength 5-10,000 psi;
 compressive strength 90,000 psi;
 flexural strength 10-20,000 psi;
 hardness 7-9 moh scale

Size	<u>Metal and Porcelain</u>		<u>Total Metal</u>			<u>Nonmagnetic Metal</u>	
	Weight, g	% of total	Weight, g	% of Metal	% of Total	Weight, g	% of Metal
Portion 1, >1680 μ	72.0	3.3	0.38	2.6	0.53	0.22	2.9
Portion 2, 840 - 1680 μ	193.5	8.9	7.09	47.9	3.66		
Portion 3, 297 - 840 μ	661.9	30.4	4.24	28.7	0.06	0.13	3.1
Portion 4, 149 - 297 μ	454.5	20.9	1.25	8.4	0.28	0.12	9.6
Portion 5, <149 μ	<u>793.9</u>	<u>36.5</u>	<u>1.82</u>	<u>12.4</u>	0.23	<u>1.18</u>	64.8
	2175.8	100	14.78	100		1.65	

contact" blade shape where the blades met in a horizontal straight line. This 0.7% may be low and in error.

Design Criteria for a Prototype Shear. From the tests made, criteria for the design of a prototype shear for operation inside a radioactive cell was determined to be:

Type	Hydraulic; horizontal, fabricated of stainless steel with "Gag"
Tonnage	300 tons
Stroke	Varying to 10 in.
No. of strokes	1 to 6 per minute
Speed	1 to 2 in./sec
Blade	
Type	Stepped punch against semicircular anvil
Hardness	Rockwell C 56-59
Alloy	Ottawa 60 (to be checked)
Clearance	1 to 3 mils
Width	1.75 in.

Collection Method for Sheared Product. Clad tubular fuel enters a chopping and leaching process as the complete fuel assembly and leaves as sheared disposable empty cylinders and metal fines from which the fissile and fertile material has been leached. The most difficult problems are:

- a. Retention of sheared product and complete recovery of particulates.
- b. Holding the last portion of the fuel assembly for the last few cuts.
- c. Collecting the chopped pieces from the shear in a bucket and transferring the container to the leacher without spread of radioactive contamination from either the shear enclosure or the bucket.
- d. Decontamination of the inner enclosure around the feed box of the shear for either maintenance or insertion of additional fuel assemblies.
- e. Providing access of acid to the fuel in the leach bucket.
- f. Transfer of leached cylinders from the leacher to disposal.
- g. Transfer of stainless steel fines from the leacher.

The simplest experimental approach is shown in schematic form in Fig. 37. It is proposed to shear from a dry isolated atmosphere into a wire mesh bucket (1000- μ openings in the wire mesh), around which an aluminum foil bucket has previously been inserted. A slide valve is closed after the bucket is filled, isolating the container from the shear. A water spray from nozzles under the valve washes off all surfaces around the underside of the valve and wets the fuel in the bucket to prevent air contamination.

Fig. 37—An experimental approach for shearing in a dry isolated atmosphere.

Access of acid to the fuel in the dissolver is accomplished by dissolving the aluminum foil in the nitric acid containing 0.005 M HgNO_3 to catalyze the aluminum-nitric acid reaction. Stainless steel fines which pass through the 1000- μ holes, are jetted from the dissolver with the uranyl nitrate dissolver product solution and removed in a feed clarification step.

2.2.3 Leaching Studies

Instantaneous dissolution rates of whole UO_2 pellets in boiling 2-13 M HNO_3 to 2 M $\text{UO}_2(\text{NO}_3)_2$ solutions and batch leaching rates of 1/2-in. to 5-in.-long chopped pieces of stainless steel-clad UO_2 in 10 to 13 M HNO_3 were measured to aid in the design of experimental leachers in the Power Reactor Fuel Processing Program. Average instantaneous dissolution rates, from 30-240 $\text{mg cm}^{-2} \text{min}^{-1}$ were found to be a linear function of the total nitrate concentration (from 7 to 15) M for dissolvents between 0-2 M in $\text{UO}_2(\text{NO}_3)_2$ (Fig. 38) and 5-12 M in HNO_3 (Fig. 39). The actual variable may be the normal boiling point temperature of the solution since the boiling points in the $\text{UO}_2(\text{NO}_3)_2$ - HNO_3 - H_2O system approximate a linear function of the nitrate molarity sufficiently well to produce the correlation observed.

Batch reaction times for leaching of UO_2 from 1/2 to 5-in.-long chopped pieces of stainless steel-clad UO_2 pellets in 150 to 200% excess of 10 M HNO_3 (2.5 to 3.0 ml/g UO_2) were determined to be 40, 70-200 (99.5% completed in 70 min), 110, 130-245 (99.8% completed in 130 min), 100 and 100 min for 1/2, 1, 2, 3, 4, and 5-in. chopped lengths, respectively (Fig. 40, Table 11). Tests included fines and separated pieces of UO_2 which varied from 30% of the total UO_2 for 1/2-in. chopped length to 2% for 5-in. chopped length. The reaction was initiated in acid at 25°C and allowed to heat to boiling. Leaching tests started at room temperature avoided extensive foaming encountered with tests started in boiling acid. In addition, comparable tests started in boiling acid required up to twice as long to reach complete dissolution. In other tests with 900% excess of 13 M HNO_3 , 1/2, 1, and 2-3/4-in. chopped lengths were completely leached in 20, 25, and 85 min, respectively (Fig. 41).

Average overall leaching rates of chopped pieces in 10 M HNO_3 varied from 0.008-0.015 g/min/g U for 5-in. chopped lengths, to 0.016-0.042 g/min/g U for 1-in. chopped lengths to 0.02-0.08 g/min/g U for 1/2-in. chopped lengths (Fig. 42). The results indicate that a considerable variation in leaching time should be expected from supposedly identical batches.

Existing data on the dissolution of ThO_2 - UO_2 pellets* in fluoride-catalyzed nitric acid ($8 < 13 \text{ M H}^+$, $0 < 1 \text{ M Th}^{4+}$) indicates leaching

*See paper by R. E. Blanco et al., this volume.

(Text continues on P.375)

Fig. 38—The effect of nitric acid concentration on UO₂ dissolution rates at various uranium solution concentrations.

Fig. 39—The effect of nitrate ion concentration on the dissolution of UO₂.

Fig. 40—Boiling HNO₃ leaching of sheared stainless steel clad UO₂ vs. time.

**Table 11. Leaching Rate of Various Lengths of Stainless Steel—
Clad UO₂ in Boiling 10 M Nitric Acid**

Volume/mass ratio: 3 ml/g UO₂

UO₂ particles dislodged from shearing included

End closure from shearing: 5 to 90%

0.370-in.-o.d. pellets clad with 0.400-in.-o.d.

0.010-in.-wall stainless steel

Sheared Length, in.	No. of Pieces	Contact Time, min	HNO ₃ , M	Initial U, g	U Dissolved, %	Reaction Rate			
						Initial	Constant	Over-all	Average
						g/min	g/min/g U	g/min	g/min/g U
0.5	24	0	10.0	175	-	-	-	-	-
		8	8.35		63	13.75	0.079	-	-
		30	7.0		93.7	-	-	-	-
		40	6.9		100	-	-	4.37	0.025
1.0	12	0	10.0	180	-	-	-	-	-
		10	9.2		38.9	3.89	0.039	-	-
		70	6.7		99.5	-	-	2.57	0.014
		200	6.65		100	-	-	0.90	0.005
2.0	6	0	10.1	175	-	-	-	-	-
		30	8.6		58.3	3.4	0.019	-	-
		90	6.9		99.5	-	-	-	-
		110	6.9		100	-	-	1.6	0.0091
3.0	4	0	10.0	183	-	-	-	-	-
		40	8.3		56.4	2.58	0.014	-	-
		130	6.3		99.8	-	-	1.4	0.008
		245	6.25		100	-	-	0.75	0.0041
4.0	5	0	9.9	266	-	-	-	-	-
		45	7.2		72.3	4.22	0.016	-	-
		100	5.8		100	-	-	2.66	0.01
		160	5.8		100	-	-	-	-
5.0	4	0	9.9	259.5	-	-	-	-	-
		55	7.1		73.2	3.46	0.013	-	-
		100	6.0		100	-	-	2.6	0.01
		160	6.0		100	-	-	2.6	0.01

Fig. 41—Nitric acid leaching of sheared stainless steel clad UO_2 vs. time.

Fig. 43—Continuous vibrating tray leacher-modified syntron spiral conveyor.

acid, allowing for observation and the connection of instrumentation, feed, and off-gas lines without introducing a load, including chopped material to be leached, in excess of 200 lb. This value is the estimated maximum load at which the conveyor will function without changing the power unit and springs.

Despite extensive test work, the vibratory spiral lift conveyor-leacher could not be operated. Mechanical failures due to poor welding and construction (a series of minute weld cracks) prevented proper consistent vibratory transfer. However, the preliminary tests with water flowing countercurrently to stainless steel pieces, both solid and shells, indicated the concept of operation to be feasible.

Continuous Inclined Rotary Leacher. Construction of a second type concept of continuous leacher of unusual design has almost been completed except for the drive unit (Fig. 44). Metal-clad UO_2 is transferred through the perforated spiral countercurrently to nitric acid leach by rotating the inner cylinder housing to which the spiral is attached. The rate will be regulated to provide UO_2 -free nitric acid-washed metal cladding for disposal at the end of the spiral. The spiral flight is perforated in a manner to effect in part a batchwise countercurrent transfer of solid and liquid phases.

Batch Leachers. A critically safe batch leacher of unusual design was designed and constructed (Figs. 45 and 46). Two 9-in.-dia outrigger arms receive and hold metal-clad chopped fuel in porous baskets, while acid from a central slab tank circulates, and dissolves the core material. Metal clad is removed in the basket for disposal; metal fines are jetted from the bottom of the outrigger arms. Provisions are included for a foam disengagement space, mixing by air sparging, feed and product lines, and necessary instrumentation. Pending the results of criticality experiments with a heterogeneous system of chopped oxide fuel and acid, the diameter of a leg of the batch dissolver was selected as 9 in.

A 1/5 scale prototype (with only one arm), constructed mainly of 4-in.-dia glass pipe with a stainless steel heat exchanger section, was tested and operated satisfactorily. Boiling nitric acid circulated through the arm and completely leached 5 kg of UO_2 from 1-in. chopped pieces of 304L stainless steel-clad UO_2 pellets in about 1 hr.

Layout of Dissolver Test Facility. A complete test facility for cold-testing and development studies was designed and installed (2nd floor, Cell 4A, Bldg. 4505, ORNL). The equipment layout in the cell (Fig. 47) and a schematic of the process flowsheet (Fig. 48) show both a continuous and a batch dissolver connected to the auxiliary equipment.

Fig. 44—Inclined drum leacher for countercurrent nitric acid leaching of UO_2 from sheared pieces of metal clad UO_2 .

Fig. 46—Prototype batch leacher for reprocessing of spent reactor fuels.

Fig. 47—Layout to perform the dissolution step in mechanical processing of spent reactor fuel elements (Bldg. 4505, cell 4A, second floor).

Fig. 48—Schematic layout of continuous spiral-vibrating and batch leachers and leacher auxiliaries.

3.0 APPENDIX

3.1 Operational Procedure For De jacketing SRE Fuel in the ORNL High-level Segmenting Facility

I. Carrier Transport Phase

1. Following an affirmative Health Physics survey of background level and surface contamination, inspect carrier and shipping equipment (Dwg. E-35518) for evidence of damage or tampering.
2. Release safety chains and hold-down fixtures on shipping rack in rail car.
3. Remove carrier, using 35-ton portable crane with adjust-a-leg sling, and place on trailer. The safety chains and adjust-a-leg sling will be provided with the trailer.
4. Transport carrier from railhead, Y-12, to Building 3026, ORNL area.
5. Lift carrier from trailer, using the adjust-a-leg sling and 50-ton hoist at Bldg. 3026. Remove trailer and place dolly (Dwgs. D-31294 and D-35498) in position under carrier. Rotate carrier 90° so that front end faces segmenting cell, and lower onto dolly.
6. Move carrier and dolly along tracks to charger door (Dwg. E-31275) face at segmenting cell.

II. Fuel Element Unloading Phase

1. Raise charger door shutter (Part 10, Dwg. E-31275) and lock in "up" position with stay rods (Part 9, Dwg. E-31275). Use 3-ton building hoist for this lift.
2. Raise carrier door and lock in "up" position with locking screws (Part 31, Dwg. D-35508). Use 3-ton building hoist for this lift.
3. From rear of carrier remove locking bolts, locking plate, shipping bolt, and plug (Parts 4, 5, 6, 7, Dwg. E-35500).
4. Insert wrench portion of carrier unloading tool (Dwg. D-35531) through plug hole at rear of carrier. Align slot with block on end of fuel storage can (Atomics International Dwg. 9693-782283), and secure wrench with bolt portion of unloading tool.
5. Move traversing table (Dwg. E-29495) to charger door face inside segmenting cell. Using Model 8 manipulators, release cover

fasteners and trough covers (subassemblies C and D, Dwg. E-37810), and swing fuel storage can cap receiver (Dwg. D-37470) onto center line of can.

6. Open inner door (Part 4, Dwg. E-31275) by means of air cylinder.

7. Insert extension portion of unloading tool into wrench. Push fuel storage can through charger door opening into cell, inserting cap in cap receiver.

8. Using either a 1/2-in.-dia rod or a ratchet wrench on the unloading tool extension, rotate the fuel storage can until the cap is free.

9. Swing cap receiver (with cap) off centerline of can.

10. Using Model 8 manipulators, attach fuel element grappling hook (Dwg. D-37467) to fuel element (Atomics International Dwg. 9693-71564) in storage can. Unwind cable from winch (Dwg. D-37474) on traversing table and attach cable to grappling hook. This is accomplished by passing the hook along the traversing table with the Model 8 manipulators.

11. Withdraw fuel element from storage can and into trough for sawing off end hardware. (Gage to locate element will be designed if needed.)

12. Disengage winch cable, and remove grappling hook and place on traversing table.

13. Close and lock trough covers.

14. Swing cap receiver and cap onto centerline of can.

15. Using tools in step 8, rotate storage can until cap is replaced on can.

16. Return fuel storage can to carrier and remove unloading tool.

17. Close inner door, and lower charger door shutter and carrier door.

This completes the operations necessary to get the first element into the segmenting cell. The remaining steps in this phase outline operations necessary to place remaining loaded cans in position for transfer into segmenting cell.

18. Withdraw detention pin (Part 8, Dwg. E-35500) and rotate

carrier rack (Dwg. E-35509) with carrier dolly ratchet wrench (Part 4, Dwg. D-35498) attached to shaft (Part A-1, Dwg. E-35509). Allow detention pin to fall into hole in rack, indicating that next fuel storage can is in position for removal.

19. Repeat steps 1 through 17.

20. After three fuel elements have been transferred to the segmenting cell, the carrier rack will be unbalanced and rack rotation may be difficult. To relieve this condition, withdraw detention pin and allow rack to rotate freely until it comes to rest.

21. Release detention pin and rotate carrier rack until loaded can is positioned by detention pin.

22. Repeat step 19 and steps 20 and 21 when necessary.

III. Fuel Element Dismantling Phase

1. Move traversing table to left, and position south end of fuel element under saw (Ty-Sa-Man Dwg. E-1136-1). Cut off end hardware and place in scrap container (Dwg. D-31299).

2. Move traversing table to right, and position north end of fuel element under saw. Cut off end hardware and place in scrap container.

3. Open trough covers.

4. Transfer fuel rods to surge rack (Dwg. D-37468) by raising lifting arms (Part 10) operated by rotary actuators (Part 7) and cams (Part 12) with controls outside cell. Lower lifting arms.

5. Using Model 8 manipulators (right hand, windows 1 and 2), remove each hydraulic cutter (Dwg. D-36335) from rack (Dwg. D-37800) and move in position over fuel rods.

6. Using Model 8 manipulator (left hand, window 1), roll fuel rod as necessary, and cut wire spacer at each end and midpoint of fuel rod. Use cutter at window 2 for cut at midpoint.

7. Return wire cutters to storage racks.

8. Using Model 8 manipulator, pull each section of wire off end of fuel rod. Using two Model 8 manipulators, bend wire section as necessary and place in scrap container (Dwg. D-31299).

9. Using 3-ton hoist, remove fuel rod lifting hook (Dwg. D-35008) from traversing table, and with assistance of Model 8 manipulator transfer fuel rod to mechanical decladder (Dwg. E-33512).

10. Return lifting hook to traversing table.

11. Each time the mechanical decladder is ready to receive another fuel rod, repeat steps 5 through 10 until all fuel rods have been processed through this phase. Omit steps 5 through 8 for center rod, which has no spacer wire around it.

IV. Fuel Rod Dismantling Phase

a. Fuel Decladding - Mechanical Decladder (Note: All cylinders and motors in this section are remotely operable from outside the cell.)

1. With the pusher hydraulic cylinder (Part 23, Dwg. E-33514), push the fuel rod to the left until it strikes the "stop" lever (Part 63, Dwg. E-33515).

2. Rotate the fuel rod with the rollers (Part 65, Dwg. E-33515) driven by the motor (Part 12, Dwg. E-33496).

3. Operate, in turn, the tube cutters (Part 67, Dwg. E-33515) at each end of the element. The cutters are moved into position and operated by rotating the handle (Part 89, Dwg. E-33515) with the Model 8 manipulator.

4. Using Model 8 manipulator, lower the tube clamp bars (Parts 93, 120, 121, 122, Dwg. E-33515) into place to secure fuel rod.

5. Move stop lever out of locating position, with Model 8 manipulator.

6. Using Model 8 manipulator, remove end plugs from fuel rod and place in scrap container.

7. Raise tube clamp bars.

8. Push fuel rod to left and into collet (Dwg. E-33511) with the pusher cylinder.

9. Lock the element in the collet with collet sleeve (Part A-27, Dwg. E-33511).

10. Energize "flushing system" (Dwg. D-33510) to flush fuel slugs out of jacket and into slug basket (Dwg. D-35010).

11. If slugs are not removed, energize pressure screw (Part A-46a, Dwg. E-33511) to force slugs out of tube.

If fuel slugs cannot be removed from jacket by procedures in steps 10 or 11, they must be removed in the auxiliary decladder. The following

steps outline procedure necessary to prepare the fuel rod for decladding in this machine:

12. Using Model 8 manipulator, remove depth gage rotating shaft assembly from storage rack (Dwg. D-37801) and install on nose guide (Part 12, Dwg. E-33514) as shown on Dwg. D-37451. Lock in position with expander (Part 14, Dwg. E-33514) by energizing compression cylinder (Dwg. D-33523).

13. Place indicator on Position 1 by operating pusher cylinder.

14. Release collet and move fuel rod approximately 1 in. toward depth gage by operating pressure screw.

15. Propel depth gage rotating shaft into fuel rod tube with pusher cylinder as far as it will go.

16. Alternately operate pressure screw and pusher cylinder so that tube is firmly supported at both ends and indicator is at Position 2. (This position indicates that the tube is internally supported by this shaft tip (Part 2, Dwg. D-37451) at this cutter.)

17. Rotate the fuel rod and cut the tubing with equipment and procedure described in steps 2 and 3.

18. Release rotating shaft assembly from nose guide de-energizing compression cylinder.

19. Using Model 8 manipulator, remove depth gage rotating shaft and fuel rod tubing from nose guide.

20. With the assistance of a second Model 8 manipulator, remove tubing from rotating shaft assembly. Place tubing in scrap basket. Place rotating shaft assembly in storage rack.

21. Place indicator at Position 1 by actuating pusher cylinder.

22. Operate pressure screw, moving fuel rod 6 to 8 in. toward compression cylinder.

23. Actuate pusher cylinder to insert nose guide into fuel rod tube.

24. Alternately operate pressure screw and pusher cylinder so that tube is firmly supported at both ends and indicator is at Position 3. (This position indicates that the tube is internally supported by a fuel slug at the cutter, and a section of tubing containing a single slug may be cut off.)

25. Rotate the fuel rod and cut the tubing with equipment and procedure described in steps 2 and 3.

26. Actuate the pressure screw and pusher cylinder as necessary, and with the assistance of the Model 8 manipulator, release the section of fuel and tubing and allow to fall in the slug basket.

If the remaining slugs in the fuel rod are against each other, they can be cut off by repeating steps 21 through 26. If the slugs are separated, it will be necessary to repeat steps 12 through 26.

If early experience indicates that slugs in the majority of the fuel rods cannot be removed by the procedures in steps 10 and 11, the following procedure will be used:

27. Repeat steps 1 through 9 with the following exception: instead of removing both end caps (see step 3), remove only the end cap nearest the collet.

28. Operate the flushing system at 750 psi (indicated by gage outside cell) to enlarge inside diameter of tube.

29. Using Model 8 manipulator, remove adapter (Part 10, Dwg. E-33514) from storage rack (Dwg. D-37801) and place on nose guide. Lock in position with expander.

30. Move adapter to left by operating pusher cylinder until end of fuel rod is fully inserted in adapter.

31. Lock end of fuel rod in adapter by turning handle screw (Part 11, Dwg. E-33514) with Model 8 manipulator.

32. Actuate the pusher cylinder and pull the fuel rod to the right until it is free of the collet.

33. Remove adapter and return to storage rack.

34. Repeat steps 1 through 11.

35. Actuate pusher cylinder to extend rod and insert nose guide into empty tube. Secure tube to nose guide with expander.

36. Draw tube out of collet by operating pusher cylinder.

37. Release expander and withdraw nose guide with pusher cylinder. Hold tube with Model 8 manipulator, if necessary.

38. Using Model 8 manipulator, move wind-up mechanism (Dwg. E-37458) into position on collet centerline and push end of fuel rod

tube into slotted cylinder (Part 4).

39. Move flattening roller (Part 9) into position by extending rod of air cylinder (Part 64).

40. Rotate coil winder by actuating air motor (Part 52) to form tube into flattened spiral package.

41. Retract flattening cylinder.

42. Eject coiled tube into slug basket by actuating ejector piston (Part 6). Retract piston.

43. Using Model 8 manipulator, return wind-up mechanism to storage position.

44. Using 3-ton hoist, remove lifting bar (Dwg. D-35010) from storage rack (Dwg. D37801) and transfer slug basket from decladder sump to drainboard (Dwg. D-35009).

45. Transfer empty slug basket from drainboard to decladder sump. Return lifting bar to storage rack.

b. Fuel Decladding, Auxiliary Slug Decladder

1. Using 3-ton hoist, remove lifting bar from storage rack and transfer slug basket from drainboard on mechanical decladder to drainboard (Part B-2, Dwg. D-36560) on auxiliary slug decladder (Dwg. E-36561). Return lifting bar to storage rack.

2. Using Model 8 manipulator, transfer fuel rod section from slug basket to decladder trough (Part B-6, Dwg. D-36560). Place in end closest to air cylinder.

3. Actuate air cylinder (Part B-1, Dwg. D-36560) with control outside cell to force fuel rod section through stripper die (Dwg. D-36559). Withdraw cylinder shaft.

4. Using Model 8 manipulator, press on fuel ejector bar (Part B-4, Dwg. D-36560), raising fuel slug and stripped jacket out of oil.

5. Using second Model 8 manipulator, transfer fuel slug from fuel ejector to slug washer basket (Dwg. D-36379). Transfer pieces of jacket to scrap basket (Dwg. D-35010). Release fuel ejector rack.

6. Repeat steps 2 through 5 until all 12 slugs from one fuel rod have been processed.

c. NaK-Oil Disposal

This operational procedure is to be issued separately and is dependent on the success of cold runs and equipment development yet to be made.

V. Fuel Washing and Canning Phase

1. Place seven empty recanning containers and lids in position in slug can storage basket (Dwg. D-36388).
2. Remove cover from tunnel hatch in operating floor of Bldg. 3026 (see Dwg. D-28461). Place tunnel transfer car in position under hatch.
3. Place storage basket and cans on transfer car platform.
4. Close hatch and move car to position under tunnel hatch in cell A.
5. Insert tunnel viewing periscope (Dwg. D-27054) through floor over tunnel in front of cell A.
6. Using 3-ton hoist in cell A, raise tunnel hatch cover (Dwg. D-36691).
7. Using 3-ton hoist, transfer storage basket from tunnel transfer car to recanning table (Part 1, Dwg. D-36678). Use periscope to view storage basket transfer from tunnel car to cell A.
8. Using Model 8 manipulator, transfer tubing coil to scrap container and fuel slugs from slug basket to slug washer basket (Dwg. D-36379). (This operation would take place on the drainboard of either the mechanical decladder or the auxiliary decladder, depending on which machine had been used.)
9. Open slug washer cover (Part 6, Dwg. E-36375) by actuating air-operated toggle clamp assembly (Part 12).
10. Using 3-ton bridge crane, transfer the basket and slugs to the slug washer.
11. Close cover.
12. Operate washer until fuel slugs have been thoroughly cleaned by the steam ejected from holes in spindle (Part 7) and spray pipe (Part 17).
13. Open washer cover.

14. Using General Mills manipulator, transfer basket and slugs to recanning table.
15. Insert General Mills manipulator fingers in can grips (Dwg. D-36670) and remove from storage rack (Part 6, Dwg. D-36670).
16. Using General Mills manipulator and grips, transfer empty can from storage basket to can loading bracket (Sub Assembly B, Dwg. D-36681).
17. Using Model 8 manipulator, remove lid from can and place on table.
18. Tilt can back so that leg rests on table.
19. Using Model 8 manipulator, transfer 12 slugs from slug washer basket to fuel can.
20. Using General Mills manipulator, return slug basket to decladder.
21. Tip loading bracket back to vertical. Replace lid.
22. Using General Mills manipulator and grips, transfer can of slugs from loading bracket to recanning machine clamp (Part 4, Dwg. D-36678).
23. Raise can against sealing mechanism by operating air cylinder (Part 20, Dwg. D-36678).
24. Operate recanning machine to seal fuel can.
25. Lower sealed can.
26. Using General Mills manipulator and grips, remove can from machine and position in front of viewing window for inspection.
27. If can is not satisfactorily sealed, return it to recanning machine and raise against sealing mechanism with air cylinder.
28. Using Model 8 manipulator, place can opener assembly (sub-assembly A, Dwg. D-36681) in position between collars (Part 9, Dwg. D-36678) on recanning machine. Insert lever (Part A-2, Dwg. D-36681) into can opener assembly.
29. Actuate recanning machine to rotate can.
30. Using Model 8 manipulator, press on lever and hold until can top has been removed by cutter.

31. Lower sealed can.
32. Using General Mills manipulator and grips, remove can and place it on the recanning table. Remove lid and place on table.
33. Repeat steps 16 through 26, using fuel slugs from the reopened can.
34. Using General Mills manipulator and grips, transfer reopened can and lid to scrap container.
35. If fuel can is satisfactorily sealed, place it in can storage basket.
36. Repeat steps 8 through 26 and, if necessary, steps through 35 until all fuel cans in storage basket are full.
37. Open cell A tunnel hatch.
38. Using 3-ton hoist, transfer can storage basket from recanning table to tunnel transfer car. Use periscope to view placing of basket on car. Close hatch.
39. Move tunnel transfer car from cell A hatch to storage cell hatch.
40. Using 2-ton hoist in storage cell, raise hatch cover (Dwg. D-36688).
41. Transfer periscope from periscope hole in front of cell A to periscope hole in front of storage cell.
42. Using 2-ton hoist, transfer storage basket from tunnel transfer car to storage cell. Use periscope as necessary to view this operation. Stack storage baskets as shown on Dwg. D-36386.
43. Close storage cell hatch.

VI. Storage Cell To Dissolver Transport Phase

(See Storage Cell Equipment Arrangement, Dwgs. D-36385, and D-36386)

1. Using 3-ton monorail crane and choker, remove shielding plug from hole in front face of storage cell. Place plug on floor to side of hole.
2. Roll modified 50-in. carrier (Dwg. D-36393) into position in front of hole. Lock wheels and open front doors.

3. Using Lee manipulator (Dwg. D-36383), place working table (Dwg. E-36392) in position under loading chute (Dwg. D-36387).

4. Move loading port shutter (Dwg. D-37182) away from hole by turning hand wheel outside cell.

5. Raise stop pin (Dwg. D-36396) at front of carrier and lock in "up" position.

6. Using a speed wrench, operate jack screw on rear of carrier (Dwg. D-36395) which places slug can guide (Dwg. D-36396) in position through cell wall and against loading chute.

7. Remove hand screw (Dwg. D-36394) from rear of carrier and insert scoop handle (Dwg. D-36394). Turn knob to screw stem into rear of loading scoop (Dwg. D-36394).

8. Push loading scoop out of carrier into cell until it hits end of loading chute.

9. Using 2-ton crane in storage cell, transfer can storage crate from storage position to working table.

10. Attach can grips (not designed) to Lee manipulator.

11. Using Lee manipulator, transfer cans from can storage crate to loading scoop, placing them end to end. After each can is placed in scoop, withdraw scoop one position so that all transfer operations take place over working table.

12. When all seven cans of fuel have been placed in scoop, withdraw it into carrier.

13. Remove scoop handle, replace hand screw, draw slug can guide into carrier, lower and lock stop pin, and close front doors.

14. Swing loading port shutter into position over hole in cell wall.

15. Move carrier to position under 50-ton hoist outside building.

16. Using 3-ton monorail crane and choker, replace shielding plug in hole.

17. Using 50-ton hoist and lifting yoke (Dwg. D-36397), lift carrier from dolly.

18. Remove dolly and place truck and skid in position under carrier.

19. Lower carrier on skid in horizontal position as shown on Dwg. D-36399.

20. Transport carrier to dissolver site at Bldg. 3019.

21. Using 10-ton building hoist and lifting yoke with stabilizing sling, remove carrier from skid and place on dissolver loading rack (to be designed, or existing rack to be modified).

22. Open dissolver loading valve.

23. Open front doors of carrier.

24. Withdraw stop pin and allow fuel cans to fall into dissolver. Insert stop pin.

25. Close front doors of carrier.

26. Close dissolver loading valve.

27. Using equipment in steps 17 through 21, return carrier to Bldg. 3026.

3.2 Time Analysis

In an attempt to determine the time required for the processing of SRE fuel clusters in the segmenting cell, one approach is to estimate the time required to process a single rod. A cluster may be introduced to the cell at any time; however, once it has been introduced to the cell, it should be fully processed without interruption, i.e., the fuel slugs should be canned and stored and the NaK and oil and scrap components suitably disposed of. The time involved is the Carrier Transport Phase (Phase I) and the Storage Cell-to-Dissolver Transport Phase (Phase VI) will not be considered in this analysis because these operations are dependent on factors not directly related to the internal workings of the segmenting cell.

The minimum time to process a single SRE fuel cluster of seven rods (69 kg of uranium) is approximately 528 min (8.8 hr) if no difficulties are encountered. If there are delays or if alternative procedures are required, the time requirements will be stated as additions to this minimum time. The estimated times for the individual phases of the SRE process are summarized below.

Fuel Element Unloading Phase. The time required to remove a single element from the carrier and place it in position for disassembly would require approximately 32 min, and this phase should be completed with a minimum of difficulty. It is conceivable that difficulty might be encountered in removing the cap from the fuel canister; however, the

cap could be removed by sawing to facilitate fuel element removal.

Fuel Element Dismantling Phase. The estimated time required to process an element through this phase of the process is 113 min. No difficulties are anticipated.

Fuel Rod Dismantling Phase. The minimum time for removal of the fuel slugs from the cladding and disposal of the cladding material is approximately 24 min per rod or 228 min for all seven rods of a single element. Time requirements beyond the minimum should be based on a single fuel rod rather than an element because the condition of the individual rods may vary, and this condition will dictate the method of decladding to be used. Because the condition of the individual rods is not known, equipment has been provided for alternative methods of removing the fuel slugs from the cladding tube. Time requirements for these methods are:

1. If both ends have been removed from a fuel rod and the slugs cannot be ejected by "flushing" or with the pressure screw, they must be processed in the auxiliary decladder. The time required for preparation and processing through this machine represents an additional 217 min per rod.

2. If experience suggests inflating the jacket before attempting to remove the fuel slugs, the time required would be 36 min more per rod than the minimum.

When the ends of the fuel rod have been removed, the NaK bonding will drain into the decladder sump which is filled with mineral oil. Processing of this NaK and oil mixture requires 308 min; however, this operation can be performed concurrently with other portions of this phase or other phases.

Fuel Washing and Canning Phase. The time required to process a single element through this phase is approximately 155 min. If a fuel can is not sealed satisfactorily, it must be reopened and the slugs transferred to another can and sealed. This operation would require 13 min additional.

3.3 Maintenance

The maintenance problems in connection with the operation of the segmenting cell may be classified as major or minor. Major problems include those for which there is not an easy and convenient solution and will probably require removal of an entire assembly from the cell for correction. All major items, except the multipurpose saw and the traversing table, will have fixtures to permit their removal through the hatch in the cell ceiling into the maintenance cubicle. Minor problems include, generally, those which require simply removal of a

defective part and installation of a replacement with a minimum of delay to the processing operation. In most cases, replacement parts will be stored outside the cell until needed to prevent their becoming contaminated or occupying needed space. The following items include maintenance problems most likely to occur and their solution:

Multipurpose Saw

a. Inoperative air motor

1. Using General Mills manipulator, loosen set screw holding motor in position.
2. Using General Mills manipulator, remove motor from base and remove from cell for decontamination.
3. Replace spare motor and adjust set screw for proper chain tension.

b. Dull or broken saw blade

1. Using Model 8 manipulator, open saw guard.
2. Lock saw motor by actuating air controls.
3. Remove nut with impact wrench.
4. Remove blade and place in scrap container.
5. Install new blade.
6. Replace nut.
7. Unlock motor.
8. Close saw guard.

Mechanical Decladder

a. Dull or chipped tube cutters (Part 67, Dwg. E-33515)

1. Using impact wrench, remove bolt (Part 66).
2. Using Model 8 manipulator, remove cutter assembly and place in scrap container.
3. Install new cutter assembly.
4. Replace bolt.

- b. Clogged flushing-system filter (Part 22, Dwg. D-37804)
  - 1. Using General Mills or Model 8 manipulator with open-end ratchet wrench, remove tubing fittings.
  - 2. Using General Mills manipulator, remove filter from rack (Part 23) and place in scrap container.
  - 3. Install new filter assembly.
  - 4. Replace tube fittings.
- c. Leaking pressure-screw O ring (Part A-18, Dwg. D-33511)
  - 1. Cut O ring with sharp knife held by Model 8 manipulator.
  - 2. Using Model 8 manipulator and wire hook, remove O ring and place in scrap container.
  - 3. Install new O ring with Model 8 manipulator.
- d. Chipped or worn expander (Part 14, Dwg. E-33514)
  - 1. Using Model 8 manipulator with a sharp knife, cut expander.
  - 2. Using Model 8 manipulator, remove expander and place in scrap container.
  - 3. Make diagonal cut on new expander.
  - 4. Using Model 8 manipulator, install expander on pressure cylinder (Part 18).

Auxiliary Decladder

- a. Burred or dull stripper die (Dwg. D-36559)
  - 1. Using Model 8 manipulator, remove defective stripper die.
  - 2. Install new stripper die.
  - 3. Decontaminate defective assembly for removal from cell for repair.

NaK-Oil Disposal System

Maintenance problems for this item have not been studied at this time.

Slug Washer

a. Clogged strainer

1. Actuate air cylinder to open strainer cover (Part 3, Dwg. D-37131).
2. Using 3-ton hoist or General Mills manipulator and "S" hook (Part 14), remove basket (Part 5) and place in scrap container.
3. Install new basket.
4. Close cover.

No maintenance problems are anticipated with other items of processing equipment in the segmenting cell while this series of fuel elements is being processed.

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SPECIAL PROBLEMS IN CHEMICAL PROCESSING AT ORNL

A. R. Irvine*

The processing of power reactor fuels at ORNL will require the solution to a number of new or especially difficult problems. These problems reflect the change in fuel element composition brought about by the demand for heat generation in a useful temperature range and at maximum emission rate, both of which are necessary to the production of economic nuclear power. This demand for economic nuclear power has led to the use of claddings which are highly corrosion resistant, to ceramic or alloy core materials because of their resistance to radiation damage, and to an increase in U-235 enrichment of core material. Each of these innovations contributes significant processing problems at ORNL, some of which are discussed below.

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1.0 CRITICALITY

The following plans for nuclear control in the ORNL Power Reactor Fuel Processing Pilot Plant have not received administrative sanction and must be viewed as tentative.

ORNL is scheduled to demonstrate recovery techniques for power reactor fuels, using as a fuel load spent assemblies from the reactors shown in Table 1. Enrichment will vary from a low of 0.35% to a high of 20%. Dissolution and solvent extraction feed preparation will be by essentially batch methods. The greatest quantities of U-235 per batch of fuel is 22 kg, which is many-fold in excess of the amount needed to sustain a thermal chain reaction.

Table 1. Enrichment and U-235 Content of Dissolver Charge

<u>Reactor</u>	<u>Enrichment</u>	<u>Batch Size, kg U-235</u>
CETR	8% in Th	22
Rural Co-op	4% in Th	12
NMSR	4.6	10.4
CPPD	3	6
Foreign Research	20	4
PRDC Blanket	0.35	0.9

In the head-end complex the dissolver and the feed adjustment tank are the items that present the most serious nuclear control problem (Fig. 1). The dissolver is to be a pipe of nominally square cross section, being about 9 in. on a side by approximately 25 ft long. Tests are in progress to determine the maximum dimension of the dissolver for CETR fuel, and results may indicate a change in the above dimension. The operation of the dissolver will be semicontinuous with respect to the aqueous phase. The average reaction rate is reduced with this type of operation as opposed to batch operation; however, the reduction in rate can be minimized by dissolving to a lower product concentration. We will attempt to dissolve to a near zero heel in order to reduce losses to decladding waste. The dissolution rate of high-density thorium-uranium pellets is very unfavorable as compared with UO_2 and uranium metal alloys, and, if the situation so demands, the acid rate will be increased beyond the current plans sufficiently to obtain a thorium dissolution capacity of 200 kg/day.

Fig. 1—Proposed nuclear control system for dissolution and feed preparation equipment in which geometry is used for the heterogeneous mixtures and soluble nuclear poisons are used for homogeneous solutions.

For dissolution of the 20% enriched Foreign Research Reactor fuels, an insert will be provided in the dissolver to maintain the metal parts in a more restricted geometry than the dissolver itself would provide. The stainless steel insert will be removed by dissolution in either sulfuric acid or aqua regia, depending on whether the Ni-o-nel or the titanium dissolver is used.

The feed adjustment tank must operate batchwise for removal of chloride from the Darex dissolver product. The feed to this vessel in most cases will be of such low U-235 content that no problem will exist before evaporation. Because the process requires evaporation to a concentration that would be supercritical, some additional control must be provided. Concentration control is impossible and batch and geometry control are prohibitively expensive in this case. Past and current practice is to use one of the controls just mentioned, with two or more means of assuring that the condition necessary to prevent criticality has been fulfilled. We are proposing, and it must be understood that this is a proposal which has not yet been accepted, to use nuclear poisons as a primary control, the addition of which is the condition which must be fulfilled to maintain $k < 1$. The quantity of boron required in a homogeneous solution is small, and the cost is negligible. We have found no reason to doubt its chemical stability in nitric or sulfuric acid systems. The amount lost by volatilization during evaporation of Thorex dissolver product is negligible. Subsequent separation of the boron from uranium and thorium by solvent extraction is not a problem. The item to be resolved is whether adequate assurance can be provided that the poison will be added as needed. It appears that procedures, interlocks, and poison monitors can all be used to provide any desired degree of assurance that the poison is added to the system.

The solvent extraction system will rely on either concentration or geometry for nuclear control in all cases except the feed and rework areas. It is expected that some of the feed solution will be delivered to the solvent extraction system in a poisoned condition, in which case this will be the sole means of control. Poisons may be used in the rework system rather than geometry control. Either batch or concentration control would be unreliable in this situation.

2.0 CORROSION

The corrosion investigations for the ORNL Power Reactor Fuel Processing program were performed by Battelle Memorial Institute until July 1959.⁽¹⁾ The effort was directed primarily toward finding satisfactory materials of construction for the following solutions:

Sulfex dejacketing	6 M H_2SO_4
Thorium dissolvent	13 M HNO_3 —0.04 M F^-
Aqua regia	5 M HNO_3 —2 M HCl
Zirflex dejacketing	6 M NH_4F —1 M NH_4NO_3
Uranium dissolvent	10 M HNO_3

The ideal material would be resistant to all these solutions; unfortunately, the metal does not yet exist which will fulfill this requirement. Two of the procedures to be used in processing power reactor fuels are two-step: different reagents are used to dissolve the clad and the core material. Each reagent is effective in dissolving only one part of the fuel element.

Stainless steel-clad thorium fuels are to be processed at ORNL by both the Darex and Sulfex processes. In both cases, the dissolver must resist attack by the thorium dissolvent, 13 M HNO_3 —0.04 M F^- . In addition, the dissolver must resist either aqua regia or sulfuric acid. Uranium oxide and some uranium metal alloy fuels require less severe dissolvents, and therefore the core dissolution phase of the process presents less of a problem for these materials. Earlier corrosion studies were directed toward finding a satisfactory material for the Sulfex-Thorex system and for the Darex-nitric acid system. This was later enlarged to include the Darex-Thorex combination and the Zirflex-nitric acid combination.

Sulfex-Thorex. Of the materials tested, Ni-o-nel appeared to be the most resistant to the two corrosion systems. The corrosion rate of Ni-o-nel in various Sulfex-Thorex solutions may be seen in Table 2. The rate of corrosion in the initial decladding and dissolving solutions is high; however, the addition of dissolution products to the corrosive media mitigates the attack on the container in both cases.

Boiling 12 M H_2SO_4 obviously cannot be used on a routine basis for depassivating because of its excessive corrosiveness.

Table 2. Corrosion Rate of Ni-o-nel* in Various Process Solutions at Reflux Temperature. Rates are in mils/month.

<u>Solution</u>	<u>Vapor</u>	<u>Interface</u>	<u>Liquid</u>
6 M H_2SO_4	1.4	5	5
6 M H_2SO_4 + 5 g/l SS	0.7	0.3	0.4
12 M H_2SO_4			4000
13 M HNO_3 — 0.05 M F^- — 0.10 M Al^{3+}	5	5	4
8.5 M HNO_3 — 0.05 M F^- , 1.0 M Th^{4+} , 0.2 M Al^{3+}	0.6	0.7	0.8

Thorex dissolvent (13 M HNO_3 — 0.04 M F^-) must contain an agent for at least partial complexing of the fluoride in order to minimize corrosion. Figure 2 shows that with no fluoride complexing agent present, the Ni-o-nel corrosion rate is ~ 55 mils/month, while the addition of 0.2 M $\text{Al}(\text{NO}_3)_3$ will reduce the rate to 2 mils/month in boiling solution. Unfortunately, the complexing agent reduces the effectiveness of the fluoride catalyst in dissolution of thorium oxide and therefore must be used sparingly. It is thought that the best compromise concentration may be 0.10 M $\text{Al}(\text{NO}_3)_3$, which will give a peak corrosion rate of 4 mils/month.

Various heat treatments of the alloy were tested in an attempt to improve its corrosion resistance. The treating temperatures varied from 1650° to 1950°F. In general, specimens that were heat-treated at $\geq 1850^\circ\text{F}$ after welding showed adequate, uniform resistance to corrosion by 13 M HNO_3 — 0.04 M F^- — 0.20 M Al^{3+} with little intergranular attack. Specimens treated at the same temperature before welding showed severe intergranular attack in the heat-affected zone around the weld. Specimens treated at 1650°F exhibited intergranular attack over the entire metal surface at a somewhat greater rate than those treated at 1850°F.

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*An International Nickel Company alloy

Darex-Thorex. While 13 M HNO_3 —0.04 M F^- (thorium dissolvent) attacks titanium in the liquid phase at a rate of ~ 10 mils/month, the addition of aluminum decreases the rate to a near-negligible value at a concentration of 0.10 M (see Fig. 2). Vapor-phase attack is also high when the fluoride is uncomplexed and also decreases sharply with the addition of a complexing agent. In the absence of a complexing agent, the vapor phase attack is general, leaving a smooth, shiny surface. With the addition of complexing agent, the general rate of attack is reduced and some localized attack (pitting) occurs, which appears to be a function of the degree of fluoride complexing. This offers considerable problem inasmuch as it is not practical to maintain a uniform degree of fluoride complexing because thorium, which is being dissolved by the solution, serves as a complexant. Figure 3 shows that corrosion in the vapor phase reaches a minimum when the solution is ~ 0.09 M in Al^{3+} and increases with either lower or higher concentrations.

Cyclic tests were performed in a titanium dissolver similar to the one used for the Sulfex-Thorex system and with a similar procedure except that 5 M HNO_3 --2 M HCl was used as the decladding agent and the duration of the decladding procedure was only 1 hr as opposed to 3. The titanium dissolver showed negligible attack except in two areas, both of which involved weldments in the vapor phase. The attack consisted of etching on the weld and surrounding heat-affected areas. Also, both these weldments involved joining either the thinner wall or condenser-tube material to the heavier flanges. Although precautions were taken to avoid contamination of the weld, such may have occurred. There was, however, no selective attack in the heat-affected zone around the weld. The carbon content of the alloy tested was $\sim 0.03\%$ with a Ti/C ratio of $\sim 27/1$. Because heat treatment after welding is undesirable due to fabrication difficulties, further tests will be made in an attempt to define the optimum conditions for heat treatment before welding.

Cyclic tests were run in a laboratory-size dissolver, using stainless steel pins containing pellets consisting of sintered ThO_2 - UO_2 . The decladding solution consisted of 6 M H_2SO_4 , which, after the reaction was initiated, was diluted to 4 M. The decladding solution was retained in the dissolver for 3 hr at the boiling point. The core dissolvent, consisting of 13 M HNO_3 —0.04 M F^- —0.04 M Al^{3+} , was used in two batches. The first batch was kept in the dissolver for 5 hr and

Fig. 2—Effect of aluminum concentration in refluxing 13 M HNO_3 containing fluoride on corrosion of Ni-o-nel and titanium in liquid phase.

Fig. 3—Effect of aluminum concentration on corrosion of titanium in 13 M HNO_3 -0.04 M F^-

was followed by a second quantity intended for final cleanup of the thorium-uranium pellets. This second quantity was retained in the dissolver at the boiling point for 3 hr.

The dissolver, the inside of which is shown in Fig. 4, was heat-treated at 1950°F for 1 hr and air-quenched after welding. Two cuts, which can be seen in the picture, were then made in the dissolver and welded back in order to compare welds made before and after heat treatment. The general corrosion rate as measured by weight loss was slightly less than 3 mils/month; however, there was general roughening of the vessel surface indicating intergranular attack. The attack rate varied from a minimum of 2.5 mils/month to a maximum of 49 mils/month in the heat-affected zone.

The rather obvious conclusions that can be drawn from the above cyclic test are that welding after heat treatment at 1950°F is not feasible and that the concentration of aluminum in the dissolution agent should be increased beyond 0.04 M to minimize intergranular attack.

Zirflex. A number of scouting experiments have been run to determine "ball park" corrosion rates of Zirflex solutions on possible materials of construction. A partial list of these materials includes Haynes 25 and 21, stainless steel types 309, 309Nb, 316, 319L, Hastelloy F, and Ti 75A. Haynes 21 showed the best corrosion resistance (2.3 mils/month in decladding solution, 2.8 mils/month in core solution) followed by 309Nb (8.5 mils/month in decladding solution, 3.4 mils/month in core solution). Stainless steel types 304 ELC, 347, and Carpenter 20 were also tested in beginning Zirflex solution (6 M NH_4F —1 M NH_4NO_3); their corrosion rates were found to be 19.7, 12, and 9.1 mils/month, respectively.

Ni-80 and 309Nb in scouting tests with initial Zirflex solutions showed high corrosion rates, which were reduced about 30% by the addition of either 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ or 0.05 M Na_2SiO_3 (rates dropped from 10 to 6.7 mils/month for Ni-80 and from 7 to 4 mils/month for 309Nb). More studies are planned for these inhibitors. There was slight intergranular attack of the Ni-80 with the inhibitors and without them; 309Nb showed slight roughening of the surfaces of the interface and liquid specimens.

Fig. 4—Cross-sectional view of Ni-o-nel dissolver after 25 Sulfex-Thorex dissolution cycles.

Ni-o-nel and 309Nb specimens were tested cyclicly in beginning Zirflex solution and core dissolvent. The cycle consisted of 3 hr in 6 M NH_4F —1 M NH_4NO_3 and 5 hr in 10 M HNO_3 —0.1 M $\text{Al}(\text{NO}_3)_3$. The corrosion rates in mils/month for Ni-o-nel and 309Nb after 11 cycles were:

	<u>Ni-o-nel</u>	<u>309Nb</u>
Vapor	3.6	2.8
Interface	1.2	0.5
Liquid	0.6	0.4

Miscellaneous. Titanium was tested in boiling mercury-catalyzed nitric acid (8 M, HNO_3 , 0.05 M Hg^{++}), to determine the suitability of a titanium dissolver for uranium-aluminum alloy fuels when the standard dissolvent is used. No harmful effects appeared during the 450 hr of the test. The corrosion rate was 0.7 mils/month.

Type 347 stainless steel was tested to see if excess chloride in solvent extraction feed would attack the columns. Stressed and unstressed specimens were placed in a mixture of organic-aqueous solutions with 3 to 10,000 ppm of chloride and held at room temperature for two years with occasional mixing. There was no apparent attack.

Additional type 347 specimens were placed in boiling 0.3 M HNO_3 , 60 g of stainless steel per liter, and 800 ppm of chloride for 912 hr. No stress corrosion was noted. However, failure occurred in the welded areas. No dependence on chloride concentration was noted. This material would not be suitable for processing equipment if solutions must be boiled for any length of time.

Type 304ELC welded specimens were tested in boiling 3 M HNO_3 , 60 g of stainless steel per liter, and 800 ppm of chloride. No stress corrosion cracking was noted but after 910 hr corrosion rates as high as 4.7 mils/month were calculated from weight loss data. However, attack was intergranular in nature so that local penetration would have been much greater than the weight loss indicated.

In the absence of fluoride, zirconium would apparently be a good material for a Sulfex dissolver. Scouting tests showed corrosion rates in 6 M H_2SO_4 to be ~ 0.1 mils/month. Its resistance to nitric acid is reported in the literature to be excellent.

3.0 PASSIVATION

Although early laboratory investigations showed no problem in initiating the reaction between Sulfex decladding solution ($6\text{ M H}_2\text{SO}_4$) and 304 stainless steel, small-scale demonstration runs with irradiated pins encountered much difficulty in this respect.^(2, 3)

The use of steel wool, as recommended by KAPL,⁽²⁾ to initiate the reaction has been proved effective, but it has the drawback of requiring attachment to each fuel assembly. The possibility that the steel wool might be omitted or become separated from the fuel assembly necessitated a search for other methods for depassivation.

In order to obtain consistent data, a procedure was developed for rapidly producing test specimens that had uniformly resistant films.⁽⁴⁾ It was found that the time required to initiate reaction on these specimens is an inverse function of sulfuric acid concentration (Fig. 5).

The effect of nitric acid on passivation is very striking. Figure 5 shows that depassivation time increases to an intolerable value with as little as 0.001 M nitrate ion. From these data it is obvious that a great deal of care must be taken to eliminate the nitric acid core solution from the dissolver before admitting the decladding reagent. Formaldehyde and formic acid are both capable of destroying nitrate. However, our information on the efficiency of formic acid for removal of trace nitrate from sulfuric acid is somewhat contradictory. One series of tests indicates excellent performance (Fig. 6), while a test run in other equipment showed no effect in 1 hr. It is believed that the nitrate ion can be satisfactorily destroyed by formic acid provided care is taken to sweep the resultant nitrogen oxides from the system. An inert purge gas probably would be helpful; introduction of oxygen from any source should be avoided.

The use of very strong sulfuric acid to break passivation unfortunately has the drawback of severely corroding the containment vessel. Tests have shown boiling $12\text{ M H}_2\text{SO}_4$ to be very effective, but the corrosion rate is of the order of 1 mil in 10 min.⁽⁵⁾ As a matter of interest, it has been shown that most of the reduction in depassivation time with increasing acid strength is due to the elevation in boiling point⁽⁴⁾ rather than the change in acid strength (Fig. 7).

Fig. 5—Depassivation time of type 304 stainless steel in refluxing sulfuric acid. Passivation treatment: 1 hr in refluxing 15.8 M HNO_3 —0.025 or 0.25 M Cr (III). Circled points refer to 0.025 M .

Fig. 6—Depassivation time of type 304 stainless steel in refluxing 8 $\underline{M}$ H_2SO_4 — HCOOH —0.001 and 0.01 $\underline{M}$ HNO_3 . Passivation treatment: 1 hr in refluxing 15.8 $\underline{M}$ HNO_3 —0.025 $\underline{M}$ Cr (III).

Fig. 7—Comparison of depassivation time of type 304 stainless steel in sulfuric acid at the boiling point, 97.5 $\pm$ 0.05°C and 88.0 $\pm$ 0.5°C. Passivation treatment: 1 hr in refluxing 15.8 M HNO_3 —0.025 M Cr (III).

4.0 SODIUM METAL BONDING

The use of a sodium metal bond between the core and cladding of fuel elements can be either advantageous or disadvantageous, depending on the method of processing. A bonding agent of this type apparently will facilitate mechanical removal of the clad, thereby minimizing waste volume. Mechanical decladding must, of course, be carried out in a manner that will exclude air and will convert the sodium to an innocuous form in a controlled fashion. This approach to the processing of alkali-metal-bonded fuels is no doubt safe; however, it is expensive, time-consuming, and as yet undemonstrated on a production basis. Therefore, other methods are being considered.

Chemical decladding or total dissolution will obviously produce violent reactions if the alkali metal bond has not been previously removed. Five test runs with approximately 5 ml of NaK in a stainless steel tube containing a glass rod proved that a detonation can occur when aqua regia is used as the dissolvent.⁽⁶⁾ The detonation took place in the fifth test and was of sufficient force to break a 3-in. Pyrex glass pipe. Three runs were made with approximately 5 ml of sodium metal in a stainless steel tube, dissolving in 6 M H_2SO_4 . No explosion occurred, although the reaction was very vigorous. In the reaction of alkali metal with both sulfuric acid and aqua regia, light was emitted (indicating combustion) which moved upward in the liquid. It is presumed that the light was coming from the reaction products as the metal was rising toward the liquid surface.

No further experiments with the aqua regia-NaK system were carried out to determine the specific cause of detonation; however, some theorizing might be beneficial. It was observed before the detonation that dissolution of stainless steel was liberating nitrogen oxides which, incidentally, could also be produced by the reaction of sodium with nitric acid. It is also known that a strong reductant can yield appreciable quantities of hydrogen even from nitrate-containing solutions. It seems possible that an explosive mixture of nitrogen oxides and hydrogen could have been produced and that this mixture was triggered by "flames" from the reacting sodium.

As far as is known, the only gaseous product of the reaction between sodium and sulfuric acid is hydrogen, which is harmless enough as

long as oxygen and other oxidants are absent. Because the reaction between sodium and sulfuric acid or any liquid must occur across an interface, the rapidity of the reaction is dependent on the interfacial area. Turbulence created by the reaction heat and gaseous products obviously increases the interfacial area, but apparently not to such an extent that an instantaneous reaction is produced. While this theorizing proves nothing, it does indicate that a possibility exists that sodium-bonded fuels can be safely declad with sulfuric acid. Such should not be undertaken without considerable "cold" testing.

Intermediate between the mechanical decladding and chemical decladding methods is one which attempts to remove the bulk of the bonding agent prior to addition of the chemical decladding agent (6 M H_2SO_4). It is thought that the sodium might be drained from a vertical tube and subsequently disposed of if each tube is ruptured at both ends and the temperature maintained above $100^\circ C$. The rupturing could possibly be accomplished either in the dissolver or else prior to loading.

5.0 DISPOSAL OF DISSOLVER OFF-GAS

Radioactive fission products must be removed from the gases released by the dissolvers in the Darex-Sulfex-Zirflex head-end facility before the gas is discharged from a stack to prevent a health hazard and disruption of ORNL air-monitoring devices and low-level counting experiments. Gaseous Kr-85 must be removed plus particulate matter containing mixed fission products. A single dissolver off-gas system will be used to treat the various fission product-containing off-gases: H_2 from a Sulfex decladding operation; NH_3 from a Zirflex decladding; and oxides of nitrogen from the Darex process.

At ORNL it will be necessary to remove Kr-85 from off-gas resulting from the dissolution of highly burned power reactor fuels, even though it is not a serious health hazard, to avoid disruption of experimental programs that are very sensitive to background radiation. Other radioactive gases, iodine and xenon, will have decayed to such a low value after the required decay time of 4-6 months that they will present no hazard or high radiation background even if they are discharged directly to a stack. The highest rate of Kr-85 evolution will occur during processing of Consolidated Edison fuel since this fuel will contain about twofold Kr-85 (11.5 curies/kg thorium) per unit

weight of fuel than other reactor fuels now assigned to ORNL. This fuel will be dissolved at an average rate of 200 kg of thorium per day and will require approximately 75 days' plant operation for the core of 15 tons of thorium. The maximum release rate of Kr-85 will occur during a decladding operation when up to 40% (1200 curies) of the Kr-85 in two fuel assemblies will be released in approximately 20 min. If this Kr-85 should be discharged directly to the atmosphere through the ORNL 250-ft stack, the average ground concentration at the maximum release rate would be approximately 1.3 times the maximum permissible concentration of Kr-85 in air; peak ground concentrations at the maximum emission rate would be approximately 100 times the MPC; and the average ground concentration over the 75-day period would be approximately 4% of the MPC. Although the average ground concentration of Kr-85 would not be sufficiently high to cause excessive personnel exposure, low-level counting experiments would be disturbed and monitoring equipment would be temporarily rendered ineffective by the spurious peak values of ground concentration.

In the proposed off-gas system (Fig. 8) particulate matter will be removed from the dissolver off-gases by a caustic scrubber followed by a filter. Kr-85 will be subsequently removed by an as yet undetermined recovery system. The fission product-containing NH_3 stream will be treated similarly except that the NH_3 will be removed early in the system either by scrubbing with water or converting it to H_2 and N_2 . The fission product-containing nitrogen oxide gas will be contacted with air to convert NO to NO_2 , scrubbed with caustic to remove the NO_2 , heated, filtered, and contacted with carbon at 400°C to convert residual nitrogen oxides to N_2 and CO_2 . The N_2 - CO_2 gas mixture will then be cooled to room temperature and scrubbed with caustic to remove the CO_2 . The residual N_2 containing the Kr-85 will be fed to the rare gas recovery system.

The danger of an H_2 - O_2 explosion in the dissolver off-gas system is to be minimized by providing a relatively leak-tight system and purging the system of potential explosive concentrations of H_2 and O_2 before and after each decladding step. An explosive mixture of air, N_2 and H_2 must contain more than four volume percent H_2 and more than five volume percent oxygen. Since impractically large volumes of N_2 or air are required to dilute the H_2 from a Sulfex decladding step below 4%, explosive mixtures in the off-gas system will be avoided by assuring that

Fig. 8—Schematic flow diagram of dissolver off-gas treatment system.

the oxygen content of the gas is below the minimum required for an explosion. During a decladding operation, the H_2 gas flow should be sufficient to dilute the O_2 from the air that has leaked into the off-gas system; when the H_2 flow becomes small, N_2 gas will automatically be added to accomplish the desired dilution. The diluent gas control valve will be actuated by a paramagnetic O_2 analyzer capable of continuously monitoring the oxygen content of the off-gas stream.

H_2 gas leaving the off-gas treatment system will probably be burned with air in a submerged combustion disposal unit in the vicinity of the head-end building, and the combustion product gases will flow from the process vessel off-gas system to the stack. Local conditions prohibit our using the simpler and possibly safer method of disposal by dilution in large quantities of ventilation air.

The danger of an NH_3 -air explosion during a Zirflex decladding step will be minimized by providing that the mixture is above the explosive concentration in NH_3 and that the temperature is above the explosive temperature for NH_3 and water-saturated air mixtures.

6.0 BUILDUP OF SOLIDS IN DISSOLVER

An accumulation of solids within a dissolver occurs if some portion of the fuel assembly is insoluble in the reagents used or time cycle considerations render it impractical to completely dissolve the cladding or core material in each cycle. Any accumulation of solids causes some additional problem in a decladding process because of added difficulty in washing when solids are present.

The case involving insoluble parts in the fuel assembly presents the greater problem to the chemical processor, in that a mechanical device must be provided to periodically remove the solids collection. Obviously, this will require an additional expenditure, which, in the case of the processing plant using contact maintenance, may be of considerable magnitude.

If structural parts of a fuel assembly are of widely varying thicknesses, the more massive pieces will probably be only partially dissolved at the conclusion of the decladding procedure. Except for the somewhat greater difficulty in washing already mentioned, no

difficulty is anticipated, as tests to date indicate that reaction will resume when the decladding reagent is added.

While it is realized that the chemical processor does not and should not dictate fuel assembly design, it is thought to be appropriate to point out that chemical processing can be accomplished more economically provided highly refractory materials are avoided and that structural materials that are soluble in a common reagent are used.

7.0 UNDISSOLVED FISSILE MATTER IN DISSOLVER EFFLUENT

Ceramic fuels are subject to breakage, attrition, and thermal fracture, which result in the production of small pieces of fuel. Processing to date has been with metal fuels that do not have the above undesirable properties. The degree of spalling which can be anticipated is unknown, for the reason that exact conditions under which all fuels will be formulated cannot be predicted. Factors that will have a bearing on the fragmentation of oxide pellets include: oxygen/metal ratio, fraction of theoretical density, irradiation temperature, and method of fabrication.

Solid fissile material leaving the dissolver in the clad solution must be collected and returned to the process stream to prevent loss of valuable material (Fig. 9). The dissolving equipment will be so designed that only particles of oxide smaller than approximately $25\ \mu$ will be carried with the clad solution stream. This separation is to be achieved by a rather simple settler. Only small amounts of oxide are expected to pass through the settler; however, that which is not removed will be trapped by a centrifuge before it leaves the building. From the centrifuge the solids will be transferred to a leach tank, where they will be treated exhaustively with dissolvent and finally transferred to the dissolver product catch tank.

During the course of core dissolution, any undissolved urania or thorium leaving the dissolver will go via the settler to a core solution surge tank, both of which will be maintained under dissolving conditions. Because these particles will be small, they are expected to dissolve in a very short time. The solids removed from this stream will be treated in the conventional way.

Fig. 9—Schematic of dissolver effluent treatment system for recovery of undissolved core material.

8.0 FEED CLARIFICATION

Feed clarification at ORNL will be accomplished by use of a centrifuge. Its selection is based on versatility, large capacity for solids, and a record of satisfactory use in radiochemical plants. Versatility and large capacity are imperative because of the diversity of processes to be accommodated and because two of the processes will yield centrifuged solids with volumes ranging from 14 to 40 gal per batch. Detracting from the centrifuge are its high cost, large volume, and mechanical complexity. While filters have received some attention at ORNL, they will not be used for the major separations because of shortcomings in the three attributes just claimed for the centrifuge. A filter system would be cheaper than a centrifuge and the solids could be washed better.

After stainless steel is dissolved in aqua regia its silica content (approximately 0.75 wt %) appears as a fine crystalline solid consisting of approximately 48% SiO_2 .⁽⁷⁾ The chloride removal step, which involves heating for a considerable time to temperatures as high as 130°C, changes the character of the precipitate from a fine crystalline solid to a flocculent material that consists of approximately 3% silica and 97% water. Laboratory tests have shown the progressive hydration of silica in a solution containing 1.2 M nitric acid, 1.8 M HCl, and 60 g of APPR fuel material per liter. The silica content of the precipitate did not go as low as the 3% just mentioned, probably because the digestion temperature was 95-100°C. It is obvious that feed clarification prior to chloride removal would be desirable because of the more desirable nature of the precipitate. However, this would entail the use of solids-liquids separation equipment resistant to aqua regia, i.e., titanium equipment. Because a titanium centrifuge would be extremely expensive and also because it would not be suitable for use in sulfuric acid-bearing solutions, it was decided to clarify this stream after chloride removal. The volume of solids produced per 100 kg of stainless steel dissolved is of the order of 14 gal.

The core solutions from declad oxide fuels are expected to contain relatively small amounts of foreign matter. The necessity for clarification of these solutions is not yet established. Hopefully, we might expect that clarification will not be required.

The Sulfex clad solution cannot properly be classified as a feed stream; however, solids-liquids separation will be required in order to allow an accurate analysis of this stream prior to discharge to waste. The volume of solids in this case will be ~ 8 gal per 100 kg of stainless steel. The character of the solids is not yet determined.

The aluminum-clad enriched uranium-aluminum alloy core fuels such as is used in Foreign Research Reactors will contain varying amounts of silica. Because silica tends to create stable emulsions, it must be removed prior to solvent extraction. It is planned to use a gelatin treatment process developed by Savannah River⁽⁸⁾ for precipitation of silica. This is carried out by adding 100 mg of gelatin per liter of dissolver solution and digesting at 85°C for 1 hr. A gelatin-silica polymer is formed which contains between 15 and 20% SiO₂ and can be readily removed by either filtration or centrifugation. Occluded uranium and plutonium are readily washed from the cake with 0.1 M nitric acid. Feed solutions clarified by this procedure are satisfactory for use in a 6% TBP-Amsco solvent extraction system as they provide a phase separation time of approximately 20 sec. It has been found that the gelatin-silica polymer is adequately stable under radiation.

9.0 EFFECTS OF THORIUM IRRADIATION PRODUCTS ON CHEMICAL PROCESSING*

The chief non-fission-product activities in irradiated thorium or U-233 are due to the U-232—Th-228 decay chain. During aqueous chemical processing of the irradiated fuel, the daughter products of this chain are removed in the first cycle aqueous raffinate stream. However, the U-232 contamination remains with the uranium product while the Th-228 contamination remains with the thorium product. Decay of these contaminants increases the significant daughter activities shortly after separation. Uranium-232 is formed during irradiation of thorium by an n,2n reaction on Th-232:

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*This section prepared by E. D. Arnold.

Both the amount produced and the U-232/U-233 alpha activity ratio increase as the irradiation exposure increases (Figs. 9 and 10). The n,2n reaction involves neutrons of energies greater than 6.37 Mev, and the effective thermal cross sections are therefore considered to be in the range of 2-13 mb. These figures show concentrations for a cross section of 10 mb. The U-232 activity and concentration in the uranium product recovered from thorium irradiated to an integrated flux of 10^{21} n/sq cm would be 1/3 of the U-233 alpha activity and 120 ppm, respectively. Since there are five additional alpha daughters in the U-232 chain, the total alpha activity of the contaminating chain could be as high as twice that of U-233 itself.

Both during irradiation and after discharge U-232 decays to Th-228 and the remainder of the chain:

The alpha-produced neutron background in U-233 is increased since many of the alpha emissions have sufficient energy to strip neutrons from light element impurities. The gamma background is increased because of the high-energy gamma of Bi-212 and Tl-208.

The major activity in recovered, recycled thorium is due to the Th-228 decay chain. Thorium-228 is formed by decay of parasitically produced U-232, with decay occurring both during irradiation and during the decay period after discharge. Since part of the Th-228 is formed during the decay period, it is possible to reduce the total Th-228 concentration by processing after as short a decay period as possible. Short decay cannot eliminate the problem, however. Continuous recycle of thorium through reactors, decay, processing, and fabrication will increase the Th-228 concentration over that formed during the first cycle. The value of the steady state concentration depends on the exact combinations of recycle conditions used, but practical considerations indicate that this value is approximately 3 times the one-cycle concentration.

In order to increase allowable irradiation levels, it becomes necessary to handle thorium that has activity levels much greater than 5 times that of natural thorium. If radiation intensities greater than 10 times natural thorium are encountered, it will be necessary to fabricate thorium elements behind several inches of lead or concrete shielding. The other alternative would be holding back the thorium stream from the Thorex process for 6 to 12 years in order to allow decay of the Th-228 to natural thorium background. The concentration and activity of Th-228 in recovered thorium at the time of reactor

discharge can be found from Fig. 10*. The Th-228 concentration after any preprocessing decay period may then be found from the equation

$$N(08) = N_D(22) \lambda_{22} \left(\frac{e^{-\lambda_{22} t_c} - e^{-\lambda_{08} t_c}}{\lambda_{08} - \lambda_{22}} \right) + N_D(08) e^{-\lambda_{08} t_c}$$

where $N(08)$ = Th-228 concentration, atoms/atom Th-232

$N_D(08)$ = Th-228 discharged concentration, atoms/atom Th-232

$N_D(22)$ = U-232 discharged concentration, atoms/atom Th-232

$\lambda_{22}, \lambda_{08}$ = radioactive decay constants of U-232 and Th-228, respectively

t_c = preprocessing decay time

The addition of isotopic contaminants that cannot be removed by conventional chemical processing seriously limits the total decontamination that can be achieved. Since these isotopic contaminants will always be present with U-233 and thorium products, and will in many cases increase with recycle or time, there is no need to decontaminate these products from fission products below a specified fraction (10-20%) of the total activity.

10.0 PLUTONIUM RECOVERY FROM FOREIGN RESEARCH REACTOR FUELS

The Foreign Research Reactor fuel assemblies are made up of curved plate-type elements composed of a uranium-aluminum alloy and clad in aluminum. The uranium is enriched to approximately 20% U-235 and after

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* The Th-228 activity in aged natural thorium is 4.1×10^3 alpha dis/sec/g Th. Thus thorium exposed to an integrated flux of 10^{21} n/sq cm at a thermal flux of 3×10^{13} n/sq cm/sec would have an activity approximately 25 times that of natural thorium.

Fig. 10—Effect of irradiation level and flux on Th-228 concentration and activity at time of discharge.

Fig. 11—A proposed method for increasing the product plutonium concentration from a solvent extraction partitioning cycle.

15-20% burnup contains less than 160 g of plutonium per reactor core. The plutonium present in the fuel, after irradiation, has a fairly high (approximately 1500 ppm) Pu-238 content. The Pu-238 concentration is not high enough to be of value for research purposes and is too high to meet our present plutonium specification because of the gamma activity. It is possible that the plutonium could be blended with large quantities of plutonium separated from low-enrichment fuels and meet specifications by dilution of the Pu-238.

Because of the uncertainty of the processing load and the small amounts of plutonium involved, we do not plan to recover the plutonium from Foreign Research Reactor fuels at this time. If the dilution procedure is acceptable and the processing load should become appreciable, it may be economical to recover the plutonium. In this event our present plans are to partition the plutonium in the first solvent extraction cycle. This plutonium would be stored and blended with the next batch of low-enrichment feed to be processed. In order to reduce the volume of solution to be stored, it has been proposed that the bulk of the partitioning column plutonium stream stripping be recycled to the extraction column and that the remainder be sent to storage (Fig. 11). In this way, the plutonium can be made to reflux in the extraction column scrub sect., thus increasing the plutonium concentration by as much as a factor of 10.

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12.0 ACKNOWLEDGMENTS

This paper is a very brief summary of the work of a large number of people. Those who participated directly in either writing or checking the paper are E. D. Arnold, W. E. Clark, J. M. Holmes, J. P. Nichols, A. C. Schafer, Jr., and L. B. Shappert.

ACCOUNTABILITY OF SPECIAL NUCLEAR MATERIAL
AT OAK RIDGE NATIONAL LABORATORY

BY

W. T. McDuffee*

1.0 INTRODUCTION

In processing power reactor fuels for recovery of fertile and fissionable material an accountability measurements program is important in maintaining nuclear safety in the plant, and maintaining process control.

After discharge from the reactor and a suitable decay period, the inactive end sections will be removed from spent fuel assemblies, after which they will be mechanically reduced, by sawing or shearing in the inactive portions, to sizes suitable for shipment. Ruptured active sections of the elements containing fertile-fissionable material may result in active debris which ultimately may be canned according to the processing site specifications and included in the fuel shipment to the chemical processing plant. Upon arrival at the chemical processing site, further handling and mechanical reduction of the spent fuel assemblies may result in additional active debris. All active debris from a given core will be processed along with the intact elements.

Although the composition of both the clad and core material from various reactors may vary, the discussion here is limited to thorium and uranium fuels clad in stainless steel. Two basic head-end processes have been developed to convert the fuels to aqueous nitrate solution required for solvent extraction:

1. The Sulfex process, in which the clad is first dissolved independently in sulfuric acid followed by dissolution of the exposed core with nitric acid.

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2. The Darex process, in which the clad and core are dissolved together in dilute aqua regia, and the chloride removed by evaporation.

A modification of the Darex process, the Darex decladding Thorex dissolution and extraction process, developed for use with thorium fuels, features clad dissolution with dilute aqua regia followed by core dissolution with fluoride-catalyzed nitric acid. After clarification to remove solids, the aqueous core and clad solutions pass to an accountability measurement station for plant input measurements. Additional measurements are made on the product and waste streams leaving the solvent extraction system, permitting a material balance on the system to be completed.

The accountability program currently in use at the Oak Ridge National Laboratory Power Reactor Fuel Reprocessing Pilot Plant is directed toward demonstrating the limits of error when determining the fertile-fissionable material content of research and power reactor fuels based on plant-input measurements. Additional data are accumulated, however, to complete the plant material balance supporting the plant-input measurements and to permit comparison of the limits of error obtainable with each method. Specifically, the accountability program described here is concerned with the measurement of the fertile and fissionable material contents of the clarified feed solutions, of the solids removed from raw dissolver solutions, and of the product and waste streams as well as the determination of the limits of error associated with each of the measurements as applied in an existing pilot plant in operation at Oak Ridge National Laboratory.

2.0 PROCESS DESCRIPTION

The position of the chemical processing plant in a typical fuel cycle is shown schematically in Fig. 1. Spent fuel from the reactor is discharged to a storage canal located at the reactor site and held for a suitable decay period. Afterward, inactive end sections are removed from the fuel assemblies, which are then partially disassembled and cut in the inactive sections, into lengths suitable for shipment to the processing site. Upon arrival at the processing site the fuel and acceptable canned active debris are unloaded to a storage canal. The active debris accepted from the reactor operator, as well as any resulting from handling of the fuel assemblies at the chemical processing site, will be collected and charged to the dissolver along with intact fuel elements.

Ultimately the choice of the head-end process may be governed by economic considerations, i. e., whether or not recovery costs of the fertile and fissionable material loss to the clad solution exceeds the "throw-away value" for that fuel. In the case of stainless steel-clad uranium fuels the Sulfex process permits separation of the clad wastes from fission product wastes, resulting in savings in high-radiation-level waste storage space. However, in the case of thorium fuels, the

Fig. 1—Power reactor fuel cycle.

Sulfex process may introduce sulfate to the core dissolution step, depressing the dissolution rate. Furthermore, destruction of all nitrate in the clad dissolution step is necessary to prevent passivation of the stainless steel.

The Darex process features co-dissolution of the cladding and core, and hence the high-radiation-level waste storage requirements are greater. However, a modified Darex process, the Darex decladding Thorex dissolution and extraction process has been developed for use with thorium fuels. It includes a preliminary decladding step with dilute aqua regia, after which the exposed core is dissolved in nitric acid catalyzed with fluoride. The cladding solutions may be discarded to waste if the losses are low. If, however, the decladding losses are too high, after chloride removal the cladding solution may be combined with the core solution and the mixture clarified and passed to the accountability measurement station.

The solids that are removed by centrifugation, settling or filtration in the clarification step are exhaustively leached of valuable material and discharged to waste. The rinses are combined with the corresponding supernatant in which the solids originated. Clarified aqueous solutions are routed to an accountability measurement station.

After the measurements are completed, the clarified feed solutions are processed through one or more decontamination cycles of solvent extraction, and the specific fertile and fissionable elements are separated and recovered as aqueous solutions. Both the aqueous product solutions and the waste streams are assayed for fertile-fissionable material content.

Product solutions may ultimately be shipped to the fuel fabricator for conversion to metal and refabrication into fuel elements, which are sent to the reactor operator for reloading. Waste solutions are sent to the disposal facilities.

In the ORNL Pilot Plant both the Sulfex and the Darex processes are to be demonstrated. Currently, however, no facilities are planned in the new head-end processing facility for processing the Sulfex cladding solutions in the event losses are high, since the Darex cladding solutions can be processed by blending with regular core solution if necessary, as already mentioned.

3.0 SPENT FUEL HANDLING

Normally the cutting, sawing, or shearing operations will be conducted in the inactive sections of the fuel elements, but owing to embrittlement, corrosion, and mechanical damage, ruptures in the active sections may occur occasionally during mechanical handling. As a consequence, fertile-fissionable material fragments may spill from the fuel elements and appear with the inactive debris generated in the saw-

ing or shearing operations. The reactor operator could collect all the active debris and package it in cans for moving provided the cans met specifications of the processing site. The cans would be resistant to corrosion by canal water but reactive to clad and core dissolvents. Although not currently scheduled at the ORNL Pilot Plant, some fuel assemblies may be further reduced by mechanical methods (resulting in additional debris) before chemical processing. It will be important that all active debris from a given core be collected, segregated, and processed during the program.

4.0 CHEMICAL PROCESSING PLANT ACCOUNTABILITY MEASUREMENTS

A schematic flow diagram for a Power Reactor Fuel Reprocessing process is shown in Fig. 2. The areas directly concerned with plant input and hence, accountability measurements, are emphasized. Additional measurements of the fertile-fissionable content of both products and waste streams are made which permit a material balance to be determined on the system supporting the plant input measurements.

Accountability measurements are those which are made to determine the total weight of fertile-fissionable material contained in a given solution, zone, vessel, or process. Chemical processing is concerned principally with aqueous solutions. To determine the total material at any location as, for example, in any given solution, it is necessary to determine the fertile-fissionable material concentration and apply these data to the volume of solution. Solution volumes may be measured by weighing the solution, determining the density, and applying this result to the total weight. Alternatively, solution volumes may be determined remotely from liquid-level and density measurements conducted in a calibrated vessel, using pneumatic instruments and correcting the data for temperature. In general, the volumes of decontaminated product solutions are determined by weighing, whereas radioactive feed and waste solutions are measured by the liquid level-density method.

4.1 Storage Canal

Accountability of unprocessed fuel stored in the canal will be maintained on a piece-count basis. The value of the accountable material in the fuel will be carried on a provisional estimate until processing has begun and accountability measurements have been completed.

4.2 Mechanical Handling and Size Reduction

During mechanical handling and size-reduction operations, any generated active debris may be collected and packaged to processing site specifications for processing along with the fuel from which it originated. No accountability measurements are contemplated on the debris itself.

Fig. 2—Power reactor fuel reprocessing.

4.3 Head End Processing

4.3.1 Decladding

In the Sulfex process the clad is dissolved separately in sulfuric acid. The clad solutions will contain variable amounts of fertile-fissionable material that must be measured prior to disposal. In general, if it develops that the fertile-fissionable material content of the clad solution exceeds the economic "throw-away value" of the fuel, it will be necessary to recover these values and the Darex process will be used.

In the Darex decladding Thorex dissolution and extraction process the clad is dissolved in dilute aqua regia and the chlorides removed by distillation. The fertile-fissionable material contained in the clad solution will be recovered by blending with the core solution produced in a subsequent dissolution step in which fluoride-catalyzed nitric acid is used as dissolvent. The clad solution may be discarded to waste if the fertile-fissionable material content is low, or after chloride removal, combined with core solution if not. The combined solutions can then be clarified and passed to the accountability measurement station. Generally, accountability measurements will be conducted on the combined mixture; however, in all cases the fertile-fissionable content of the clad solutions will be determined.

4.3.2 Core Dissolution

In the Sulfex process the exposed core is dissolved in nitric acid. In processing of thorium fuels by either the Sulfex or the Darex decladding Thorex dissolution and extraction process, fluoride catalyst is included with the nitric acid core dissolvent. In the straight Darex process, limited to uranium fuels, both the clad and core are dissolved simultaneously in dilute aqua regia. The clad-core solutions are processed through one or more cycles of evaporation to remove chlorides. After adjustment to approximate solvent extraction flowsheet feed specifications, the solution is clarified to remove solids and sent to the accountability measuring station described below.

4.3.3 Clarification and Solids Assay

Solids varying widely in quantity, chemical composition, and physical behavior appear in both clad and core solutions. These, because of their interference in the operation of the solvent extraction system, must be removed. When the solids are removed by centrifugation or filtration, both dissolved and sorbed core material will be carried with the cake. Rinsing the cake removes dissolved core material; however, sorbed material requires exhaustive leaching before the solids may be discarded to waste. Rinses and leaching solutions are added to the supernatant. Solids containing refractory fines of core material may be slurried and recycled to the dissolver in a subsequent run.

The assay of solids presents a serious problem in obtaining representative samples and accurate analyses. The most promising general approach to the problem appears to be to slurry the cake, transfer the slurry to a tank, and exhaustively leach the residual core material from the solids. As an alternative method, a sample of the slurried solids might be removed, the volume ratio of liquid to solids determined, and the solids then assayed for fertile-fissionable material and the total loss determined. Despite the imprecision likely in such a method, if the fertile-fissionable material content is low, the contribution to the total error in measurement may be small enough to be acceptable.

4.4 Plant Input Measurements

Plant input will be measured by totaling the fissionable-fertile material determined from assays of the following streams applied to measured quantities of solution or solids:

1. Condensate from the dissolver off-gas condenser
2. Solids removed from both core and clad dissolver solutions
3. Core and clad dissolver solutions

4.4.1 Volume Measurements

The volume of the clarified highly radioactive dissolver solution will be measured in a calibrated accountability measurement vessel.

Accountability Measurement Vessel. Shown schematically in Fig. 3 is the accountability measurement vessel as installed in the Oak Ridge National Laboratory Power Reactor Fuel Reprocessing Pilot Plant. Located inside heavy shielding, it consists of a 2000-liter vessel with a reversed dish bottom and standard dish top. It is equipped with (1) dual lines of pneumatic instrumentation for remotely indicating and recording liquid level and density; (2) temperature indicator; (3) air sparger; (4) heat transfer surfaces; and (5) a recirculating sampler. The instrument assembly of this vessel receives special maintenance for sensitivity, response, linearity, and detection of drift from zero. A permanent manometer installation permits rapid precise measurement of both primary and the amplified signal for comparison with the indicated readings.

Calibration. The vessel was calibrated with both water and an aqueous uranyl nitrate solution of approximately dissolver solution composition. Weighed increments of solution were added and the corresponding liquid-levels noted. Similarly, weighed amounts of solution were removed from the vessel and a second calibration was made. Plotting of these data gave two curves, one for filling and another for emptying (Fig. 4). The curves almost coincide at the 1600-liter volume (40% true liquid level) but diverge at the lower volumes; at the 400-liter volume (true liquid level 4%) the difference in the two curves is ~18.5 liters. The limit of error for both calibration curves (Fig. 5) was twice as high in emptying the vessel as in filling; at 400 liters the limit of error is 0.7% for filling and 1.3% for emptying, while at

Fig. 3—Schematic view of S-2 instrumentation.

Fig. 4—Calibration of S-2.

Fig. 5—Limits of error curves for S-2 vessel calibration.

1400 liters the limit is 0.2 and 0.3%, respectively. However, in a typical transfer of 1000 liters, taken as the difference in the 1400- and 400-liter volumes measured while emptying the tank, the limit of error for a single measurement is ± 0.5 per cent.

Homogeneity. Homogeneity is ensured by air-sparging the solution for 1 hr minimum. It was found by experiment that in overlaying 900 liters of uranyl nitrate solution of 200 g/liter with 250 liters of uranyl nitrate solution of 360 g/liter, adding 250 liters of water, air sparging the mixture for several successive 15-min intervals sampling after each, no change in composition was detectable within the limits of experimental error after the first 15 min of sparging.

Sampling. Representative samples are withdrawn from the accountability measurement vessel by means of a recirculating sampler that features the airlift principle. It was determined experimentally that representative samples are withdrawn after about 15 min of recirculation. In normal practice three samples are withdrawn. The first (most likely to be contaminated) is discarded and the second and third submitted for analysis.

Analytical Procedures. The analytical procedures to be used in determining the fertile-fissionable material content of core and clad solutions are shown below along with the limits of error:

Uranium, natural and depleted ($< 1\%$ combined U-235-U-233): Spectrophotometric ammonium thiocyanate method; limit of error ± 4 per cent; (the coulometric method under development promises limits of error of about ± 1 per cent).

Uranium, enriched: Automatic potentiometric ferric sulfate method; limit of error ± 0.2 per cent.

Thorium: Spectrophotometric thoron method; limit of error ± 2 per cent.

Plutonium: Thenoyltrifluoroacetone (TTA) extraction method; limit of error ± 2.5 per cent (requires that the specific activity of the plutonium be known). The coulometric method now under development is expected to result in limits of error of about ± 1 per cent.

Isotopic assay: The isotopic ratios of uranium and plutonium are determined by mass assay by the thermal emission method. The limit of error by direct measurement is ± 0.01 per cent for uranium isotopes and ± 0.5 per cent for those of plutonium.

4.5 Plant Output

Plant output will be determined from accountability measurements of the fertile-fissionable content of the recovered products and waste

streams. Approximately 99 per cent of the fertile-fissionable material processed in the plant is recovered as product and about 1 per cent appears in the waste streams.

4.5.1 Volume Measurement

Product Solutions. The volume of product solutions will be measured by applying laboratory-determined density measurements to weighed quantities of solution; limit of error, ± 0.3 per cent.

Waste Solutions. The volume of waste solutions will be determined from liquid-level and density data obtained with the remote pneumatic-type instruments installed in the plant catch tanks; limit of error, ± 2 per cent.

4.5.2 Analytical Procedures

Product Solutions

Uranium (all enrichments including U-233): Automatic potentiometric ferric sulfate method; limit of error ± 0.2 per cent.

Thorium: Spectrophotometric-thoron method; limit of error, ± 2 per cent.

Plutonium: Potentiometric ceric sulfate method; limit of error, ± 0.5 per cent.

Waste Solutions. Highly radioactive waste solutions will be analyzed for fertile-fissionable material content by the following methods:

Uranium (all enrichments): Fluorimetric method; limit of error, ± 10 per cent (< 0.01 g/liter).

Thorium: Spectrophotometric-thoron method; limit of error ± 2 per cent.

Plutonium: Thenoyltrifluoroacetone method; limit of error ± 15 per cent (< 0.0001 g/liter). The specific activity of the plutonium can be satisfactorily estimated from the irradiation history of the fuel.

Uranium-233: Hexone extraction method; limit of error ± 15 per cent (< 0.0001 g/liter); requires that the specific activity of the uranium be known.

4.6 Accuracy

Plant Input. The over-all limits of error in plant input measurements are currently estimated to be thorium ± 2.5 per cent, uranium ± 3 per cent, and plutonium ± 3 per cent.

Plant Output. The limits of error in determining program balances based on product-plus-loss measurements are estimated to be throrium ± 2 per cent, uranium ± 0.5 per cent, and plutonium ± 0.8 per cent.

5.0 PROBLEMS

A number of problems currently exist or are anticipated in the accountability phase of the Power Reactor Fuel Reprocessing Program. Satisfactory solutions to these problems should be developed to improve not only the accuracy of the accountability measurements, but also to improve process control and ensure nuclear safety. Some of the more pressing problems are discussed below.

5.1 Canal Debris

Canal debris containing fertile-fissionable materials may be generated during fuel element assembly, handling, disassembly, and cutting, can lead to shipper-receiver differences that may be difficult to resolve if all active debris is not carefully collected and processed along with the bulk of the fuel. Since active debris will probably be generated both at the reactor site and also in carriers during transit as well as in the chemical processor's canal, the adoption of good housekeeping practices at both sites is emphasized in collecting, monitoring, and segregating all active debris and processing this along with the intact fuel assemblies from a given core.

5.2 Sampling

The two problems most frequently encountered in sampling are inhomogeneity in the solution sampled and withdrawal of nonrepresentative samples. Homogeneity of solids-free solutions can be assured by adequately mixing or sparging the solution. Special care should be taken when high density solutions are diluted with lighter ones. Most sampling devices withdraw the sample from near the bottom of the vessel; large errors can be made in estimates of the total material content of solutions based on analyses of samples withdrawn from a mixture of a heavy and a light solution when incomplete mixing has occurred.

With solutions containing suspended solids, particularly those which show surface absorptive properties such as the siliceous solids expected with many reactor fuels, there appears to be no generally acceptable method of obtaining homogeneous samples. The condition is aggravated further when such solids show some degree of selectivity for one of the fissionable substances in its sorptive behavior. The best approach to this type of problem appears to be in recognizing that such a problem exists and in chemically destroying the sorptive property of the solids. Fortunately, accountability measurements of this type occur mostly in the case of solids-containing waste solutions where the fertile-fissionable material content is very low; feed solutions, as

already mentioned, will be clarified prior to conducting the measurements. However, determining the fertile-fissionable material content of solids is of necessity an integral part of an accountability program based on plant input measurements.

As already indicated, the separated solids must be assayed. Currently it appears that radioactive solids can be sampled only by slurrying and sampling the slurry. The ratio of solids to liquid in the slurry sample can be estimated upon centrifuging and used in applying the results of chemical analyses of the solids to the total volume of slurry in determining the total fertile-fissionable material content.

Nonrepresentative samples occur usually as a result of contamination after the sample has been withdrawn; however, it may occur also during withdrawal. Strict observance to recommended recirculating procedures will ensure clearing the sampling devices and minimize the probability of contamination during withdrawal. This does not guarantee freedom from contamination from outside sources during subsequent handling, however.

Sampling of aqueous solutions at elevated temperatures results in samples with a slightly higher concentration of dissolved material than in the solution being sampled. This condition is most likely to occur with samplers using the airlift principle where the suction head is relatively high.

5.3 Analytical

The most persistent problem that occurs with respect to analytical data is that of "out-of-control" analyses. This problem can be minimized by maintaining a quality control program in the analytical groups.

5.4 Plant Clean-out

At the conclusion of a program it is necessary to purge the process equipment of fertile-fissionable material, both to recover the material (completing the campaign balance) and to prevent cross-contamination of the material to be processed in the program that follows. Waste losses are higher during this phase of the program, and in short experimental programs these losses contribute significantly to the overall loss. Off-specification products often are recovered that must be reprocessed; decontaminating reagents that interfere with solvent extraction operation are produced that require reprocessing for fertile-fissionable material recovery. The fertile-fissionable materials in such clean-out solutions usually occur in low concentrations, where analytical accuracy is decreased.

OAK RIDGE QUESTION AND ANSWER SESSION

Baranowski:

We have just one question regarding the Oak Ridge presentation and it is addressed to Clyde Watson.

"If you have a receiving pit for the cask and a bridge-mounted saw in the same pit, how do you avoid unnecessary gross contamination of the cask when operating the saw directly above the cask? Further, is the cask lowered into a water-filled pit?"

Response - C. D. Watson:

Answering the questions in reverse, yes, the cask is lowered into a water-filled pit, thirty-five feet deep. Normally, we would not schedule a sawing operation while the cask is in the pit.

We would avoid the spread of particulate contamination throughout the canal, we hope, by placing a tray underneath the saw. Water will be withdrawn from a central portion of the tray, brought through a settling tank, and then pumped through a sand filter, or some comparable filter, and the water returned to the canal or sent to waste storage depending upon the success one has with removing the particular matter.

Again, I point out that this is still a matter of development, and we don't know exactly what the equipment looks like at this time. In any event, the sawing operations and the unloading operations will be scheduled such that both operations do not occur at the same times.

ATTENDANCE LIST

OFF-SITE ATTENDEES AT AEC SYMPOSIUM

Dr. D. H. Ahmann	G. E. - Vallecitos Atomic Lab. Pleasanton, Calif.
Dr. Yumi Akimoto	Univ. of Calif. - Lawrence Radiation Lab. Berkeley, Calif.
B. Anderson	AEC - Chicago, Ill.
E. L. Anderson	AEC - Washington, D. C.
J. D. Anderson	State of New York, Albany, N. Y.
Ralph J. Atkins	Nuclear Materials & Equipment Corp. Apollo, Pa.
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Samuel Edlow	Edlow Lead Co., Columbus, Ohio
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D. J. Pflaum	AEC - Washington, D. C.
Norman D. Phillips	Babcock & Wilcox Co., Lynchburg, Va.
G. F. Quinn	AEC - Washington, D. C.
H. K. Ray	AEC - Washington, D. C.
A. Redon	Eurochemic - France
Edward N. Rein	Willamette Iron & Steel Co. Portland, Ore.
Dwight Richards	Willamette Iron & Steel Col Portland, Ore.
O. T. Roth	AEC - Washington, D. C.
W. E. Rowe	Minnesota Mining & Manufacturing Co.
K Saddington	Windscale Works United Kingdom AEA
G. Salzano	Vitro Corp., New York, N. Y.
W. D. Sandberg	AEC - Savannah River Plant Aiken, S. C.
Dr. W. S. Schuller	Euratom - Germany
Patrick J. Selak	Kaiser Engineers, Oakland, Calif.
F. T. Selleck	Fluor Corp., Ltd., Los Angeles, Calif.
Rodman A. Sharp	General Atomics, San Diego, Calif.
George Sherrerd	Bird Machine Co., South Walpole, Mass

Dr. Robert Simon	General Atomics, San Diego, Calif.
A. B. Sissons	Commonwealth Edison, Chicago, Ill.
L. J. Sloggy	C. F. Braun & Co., Alhambra, Calif.
Sam Sobal	AEC - Washington, D. C.
R. E. Stanford	Detroit Edison, Detroit, Mich.
C. E. Stevenson	Phillips Petroleum, Idaho Falls, Idaho
A. Stewart, Jr.	National Lead Co., Albany, N. Y.
John Stolz	Atomics International, Canoga Park, Calif.
H. A. Sturza	Allis Chalmers, West Allis, Wisc.
Peter Suter	Eurochemic - France
D. H. Swanson	AEC - Idaho Falls, Idaho
M. H. Thomas	AEC - Washington, D. C.
F. H. Tingey	Phillips Petroleum, Idaho Falls, Idaho
G. W. Tompkin	Mallenkrodt Nuclear Corp., St. Louis, Mo.
W. F. Tuff	Haynes Stellite Co., Seattle, Wash.
T. Tuohy	Windscale Works United Kingdom AEA
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J. O. Vadeboncoeur	Sylvania-Corning Nuclear Corp. Burlingame, Calif.
J. Vanderryn	AEC - Oak Ridge, Tenn.
R. D. Walton	AEC - Idaho Falls, Idaho
F. H. Warren	Pickard-Warren-Lowe Associates Washington, D. C.
C. D. Watson	Union Carbide Nuclear, Oak Ridge, Tenn.
Dr. B. Weidenbaum	G. E. - Vallecitos Atomic Lab. Pleasanton, Calif.
Whitney Weinrich	Weinrich & Associates, Washington, D. C.

J. A. Weissenfluh	Babcock & Wilcox, Lynchburg, Va.
H. V. Werner	AEC - New York Operations Office New York, N. Y.
W. F. White	Bird Machine, South Walpole, Mass.
B. W. Wilkinson	Dow Chemical, Midland, Mich.
Rudolph Winkler	Eurochemic - Germany
L. L. Wyman	U. S. Bureau of Standards Washington, D. C.
C. Yerkes	Virto Corp., New York, N. Y.
V. A. Zora	Blaw-Knox, Pittsburgh, Pa.

HANFORD ATTENDEES AT AEC SYMPOSIUM

Includes those who attended only part of
the meetings and/or the dinner meeting.

F. W. Albaugh	L. A. Hartcorn
G. J. Alkire	O. F. Hill
C. R. Anderson	D. W. Hoba
J. Atwood	J. F. Honstead
	H. H. Hopkins
R. G. Barnes	
O. F. Beaulieu	E. R. Irish
G. E. Benedict	R. E. Isaacson
S. R. Bierman	
H. T. Blaine	T. W. Jeffs
J. A. Bloom (AEC-HOO)	R. F. Jimenez
L. B. Bradley	W. E. Johnson
L. P. Bupp	W. H. Johnson
R. E. Burns	J. W. Jordan
	B. F. Judson
M. H. Campbell	
H. A. Carlberg	F. T. Keenan
J. T. Christy (AEC-HOO)	R. A. Kennedy
V. R. Cooper	C. E. Kent
J. J. Courtney	G. R. Kiel
P. A. Craig (AEC-HOO)	P. S. Kingsley
D. D. Deming (AEC-HOO)	T. G. LaFollette
J. P. Derouin (AEC-HOO)	W. A. Lampton (AEC-HOO)
R. W. Doerr	C. E. Linderoth
V. D. Donihee	
R. P. Dragoo (AEC-HOO)	D. V. McLenegan
J. P. Duckworth	W. K. MacCready
	W. N. Mathis
J. B. Fecht	R. W. McKee
C. B. Foster	P. R. McMurray
H. R. Freitag (AEC-HOO)	L. M. Meeker
	L. R. Michels
I.M.A. Garcia	W. N. Mobley
R. G. Geier	R. H. Moore
A. T. Gifford (AEC-HOO)	
C. T. Groswith	J. L. Nelson
G. L. Gurwell	J. B. Nesbitt
W. R. Hamilton	M. L. Oldfather
W. M. Haney	R. E. Olson
G. L. Hanson	
K. M. Harmon	H. M. Parker
M. K. Harmon	L. F. Perkins (AEC-HOO)
R. W. Harmsen (AEC-HOO)	A. M. Platt

W. H. Reas
C. L. Robinson (AEC-HOO)
A. L. Ruiz
M. J. Rutherford

H. H. Schipper (AEC-HOO)
W. C. Schmidt
R. A. Schneider
W. W. Schultz
H. P. Shaw
D. F. Shepard
M. J. Shepherd (AEC-HOO)
C. J. Shortess
J. M. Skarpelos
R. J. Sloat
N. A. Smith
P. W. Smith
W. S. Sterling (AEC-HOO)
C. D. Swanson
W. H. Swift
W. O. Switzer

H. F. Tew
R. E. Tomlinson
J. E. Travis (AEC-HOO)

A. J. Waligura
M. T. Walling
J. H. Warren
M. F. Wiitala

M. E. Yates

L. L. Zahn