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TRANSURANIUM QUARTERLY PROGRESS REPORT
FOR PERIOD ENDING AUGUST 31, 1963

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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CHEMICAL TECHNOLOGY DIVISION
METALS AND CERAMICS DIVISION
PLANT AND EQUIPMENT DIVISION
REACTOR CHEMISTRY DIVISION
PLANT ENGINEERING, ORGDP

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PERIOD ENDING AUGUST 31, 1963

Compiled by
W. D. Burch

MARCH 1964

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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1. ABSTRACT

The development of processes to separate and purify the transuranium elements, process equipment development, HFIR target fabrication studies, design of the TRU Processing Plant, design and installation of development facilities, corrosion studies, and analytical research directed toward this program are reported here.

The significant developments and accomplishments of this period include: (1) a demonstration of the Tramex flowsheet at a feed activity level of 10 w/liter in batch countercurrent tests; (2) the discovery that small quantities of methanol in the feed to the Tramex process appear to alleviate the problem of acid loss by radiolysis; (3) the preliminary development of a new chemical system, free of chlorides, for the separation of lanthanides and actinides, which may have application to the Transuranium Program; (4) the successful fabrication of six prototype HFIR target rods for irradiation testing; and (5) the start of construction of the Transuranium Processing Plant on July 1.

Development of Chemical Flowsheets for Overall Process. -- A series of five countercurrent solvent extraction tests were made of the Tramex flowsheet with Cm^{242} power densities varying from 5 to 10 w/liter. No adverse effect on the extraction process was noted due to alpha radiation, and the results indicate that the Tramex process can achieve both high recovery of transplutonium elements and high decontamination from fission products.

The principal effect of alpha radiation in Tramex feed is a loss of acid at the rate of about 0.1 mole per liter per day at activity levels of 10 w/liter. Since Tramex process separations are greatly affected by small changes in acidity, methods for controlling this acid loss were studied. Reducing agents such as formaldehyde and methanol were effective in preventing acid loss. Ten volume percent methanol in 10 M LiCl containing 18 w of Cm^{242} per liter maintained the acid concentration between 0.03 to 0.06 M for 25 days. Additional studies are in progress to determine the effect of methanol on the Tramex extraction process.

Equilibration of Tramex feed with inert gas containing a reduced partial pressure of hydrogen chloride was also investigated as a method for controlling feed acidity. Results indicated that feed acid could be maintained in the desired range when the feed temperature was elevated to 120°C, but difficulties attendant with maintaining feed at this temperature make this method of acid control unattractive.

The addition of small amounts of Alamine 336·HNO₃ to Alamine 336·HCl-DEB was investigated as a possible means of increasing actinide distribution coefficients. It was hoped that with higher distribution coefficients, the control of Tramex feed acid would be less critical. However, the extraction in the chloride-nitrate system is even more sensitive to free acid than in the all-chloride system.

Laboratory demonstrations of the conversion of Cm²⁴² product solutions from chlorides to nitrates by adding nitric acid to remove the chloride were made in 1/10-scale tantalum equipment with simulated feed. Effective chloride removal was obtained; however, the nitric acid concentration of the final product was about 15 M. Ruthenium did not volatilize during the conversion, but volatile RuO₄ was formed when small quantities of NaBiO₃ were added to the boiling 15 M HNO₃.

The use of spring-loaded ion exchange columns improved column operation during Am²⁴¹-Cm²⁴² separations at activity levels of 50 w/liter. The effect of gassing was thereby controlled, and separation of the resin bed was prevented. Lithium chloride anion exchange was successfully used to recover and purify americium-curium containing 22 mg of Cm²⁴² and to separate gram quantities of Am²⁴¹ from contaminant rare earths. These products are being used in current development work.

Seventy-nine grams of high-fired PuO₂ in the desired particle size range (-70 to +325 mesh) was prepared for use in prototype HFIR targets. Several methods of preparation were investigated. Methods to recover plutonium from HFIR target rejects were also investigated.

Alternative Extraction Method for the Separation of Lanthanides from Trivalent Actinides. -- A new method that is being developed for the separation of the lanthanides from the trivalent actinides gives separation

factors of about 100 between the least extractable lanthanide and americium. It consists of extracting the lanthanides by a monoacidic organophosphate or phosphonate in an aromatic diluent from a mixed solution of a carboxylic acid and an aminopolyacetic acid complexing agent. A suitable extractant is a diisopropylbenzene solution of di(2-ethylhexyl)-phosphoric acid, and a suitable aqueous phase is 1 M lactic acid containing 0.1 M pentasodium diethylenetriaminepentaacetate, the complexer for the trivalent actinides. The trivalent actinides may be recovered subsequently from the aqueous phase by oxalate precipitation or by extraction with a stronger extractant such as an n-dodecane solution of 2-ethylhexyl-phenylphosphonic acid, followed by stripping with nitric acid. Neither nitrate salts nor any reasonable amount of radiation absorption interferes with the separation.

The higher extractability of californium and the heavier actinides makes their separation from the lanthanides considerably more difficult than the separation of americium and curium from the lanthanides.

Extraction of Americium(VI). -- Tracer level Am(VI) was usually less extractable than Am(III) in several extraction systems. Extraction by di(2-ethylhexyl)phosphoric acid from dilute nitric acid showed a preference of 10^4 for Am(III) and indicated a possible new method for preferential extraction of Cm(III) from Am(VI).

Experimental Engineering Studies. -- The design concepts and process equipment important to the processing facility are being tested in a full-scale cell mockup. Tests of procedures for replacing the equipment, which depend on use of disconnects, equipment racks, and an equipment transfer case, were continued. An improved cell lighting system was developed. Procedures for replacing manipulator booting and "alpha" windows were tested. The system and procedure for removing and replacing resin in an ion exchange column was demonstrated.

Pulsed columns were tested for the scrubbing of europium tracer from 30% Alamine 336 (the most difficult part of the Tramex process). The average stage height of 17 in. and total throughput of 12 ml/min at 50°C, 40-cpm frequency, and 0.2-in. amplitude were not appreciably improved for other conditions tested. All tests were performed in 3/4-in. glass columns equipped with tantalum plates (5% free area) on 1/4-in. spacing.

Four of 54 protective coatings tested at a dose of 4×10^9 r of gamma radiation were still serviceable after exposure in deionized water, and 29 after exposure in air. Decontamination factors by a simple water flush and a 3 M HNO_3 scrub averaged 1850 for polyesters, 990 for vinyls, 870 for epoxies, and 410 for modified phenolics.

Target Fabrication Design and Development. -- The problem of achieving cermet pellets of the desired density and acceptable thermal conductivity has been solved. About 200 good pellets were produced for the prototype target rods. The design of the joint for welding the end closures was modified, and procedures were developed by which very good welds can be made in glove box operations, but the problem of consistently achieving a high-quality weld by remote operation has not been completely solved. Six prototype target rods containing PuO_2 were made in a glove-box line, and four of these are being irradiated in the Materials Testing Reactor.

Conceptual design, construction, and operational checking of the equipment for the three cubicles in the TRU facility are proceeding on schedule. The major effort was placed on cubicle 3 since it is considered the most difficult task and it is nearest to completion. Cubicle 1, considered to represent the easiest task, received the least attention.

Design of Processing Plant and Equipment. -- Installation of equipment in the "hot" development facility, cell 4 of Building 4507, was almost completed, and cold startup operations were begun. Design of the supporting equipment in cell 3, including a dissolver and work space for laboratory-type equipment is proceeding. A carrier-unloading station, which will permit the transfer as a nitrate solution of the americium-curium-rare-earth fraction from the Savannah River TRU irradiations into an underground storage tank outside Building 4507 was designed, built, and installed.

Design of the chemical process equipment for the facility is about 33% complete. Sixteen engineering flowsheets and 47 equipment drawings were approved and issued. Major equipment items for which design was completed are: the process samplers, the dissolvers, cubicle-to-pit disconnect well and line-bundle structure, and the first-cycle solvent

solvent extraction equipment rack. The intercell piping concept, including remotely replaceable Zircaloy-2 waste and off-gas headers, was completed and detail design started. Design modifications to the disconnect clamp were made in order to provide a positive opening and closing action and to facilitate remote removal and replacement of the top clamp and bolt assembly.

The lump-sum contract for the processing plant was let to Blount Brothers Construction Company, and notice to proceed with construction was given, effective July 1. Since that time, installation of underground piping has been well advanced, and excavation for the cell bank has been completed. Procurement by ORNL of critical items for installation by the building contractor, and the design and fabrication of mechanical equipment for the building is proceeding on schedule.

A complete re-evaluation of the ORNL design Critical Path Schedule and manpower requirements was made in July, including redrawing of all arrow diagrams. A significant increase in estimated design manpower resulted, but no change was made in the overall schedule.

Corrosion Studies. -- Since certain parts of the process equipment will contain mixtures of nitric and hydrochloric acids as well as the separate acids, a program to study corrosion rates on both Zircaloy-2 and Hastelloy C in these acid environments was undertaken and completed this quarter. The addition of enough nitric acid to 3 M HCl to make the mixture 0.5 M in HNO_3 had relatively little effect on the corrosion of either metal, but similar concentrations of nitric acid in 6 M HCl drastically increased the corrosion rate of Hastelloy C (up to 100 mils/month at 43°C) and raised the rate on Zircaloy-2 at the boiling point from 0.2 to 1.6 mils/month. Zircaloy-2 has satisfactory corrosion resistance to all concentrations of nitric and hydrochloric acid at 43°C, but confirmatory tests showed that hydrogen pickup and embrittlement severely limits its use at boiling temperatures. Tests with Zircaloy-4 showed it in general to be less corrosion resistant than Zircaloy-2.

Two tantalum-plated specimens remained in good condition after exposure to boiling 6 M HCl for 1300 hr, although one developed a blister defect

at the interface between two layers of tantalum plate. Hastelloy C corroded at less than 0.1 mil/month in all TRU organic media at 43°C. Homalite Cr-39, an allyl diglycol carbonate plastic used in the fabrication of the mixer-settlers for the Building 4507 development facility, was severely attacked in both 6 M HCl and 8 M HCl at 55°C, although it was quite stable in 10 M LiCl--0.1 M HCl.

Development of Analytical Methods. -- A direct, nondestructive method for the determination of Cf²⁵² by gamma scintillation counting of the prompt gamma has been developed. As little as 10⁻² nanograms of Cf²⁵² can be quantitatively measured. Studies of the applicability of polarography to the measurement of free acid and aluminum in LiCl solutions were undertaken, and the spectrophotometric determination of the rare earths, thorium, and zirconium with Arsenazo III was evaluated.

2. INTRODUCTION

Gram quantities of transuranium elements for research uses are to be produced in the High Flux Isotope Reactor (HFIR) and Transuranium Processing Facility (TRU) being built at Oak Ridge National Laboratory. Production of these elements in quantity will simplify research with them and make it possible to enlarge our knowledge of their chemistry, solid-state physics, and metallurgy. Target material will be provided for production of still heavier and unknown elements.

Isotopes of curium, berkelium, californium, einsteinium, and fermium will result from irradiation in the HFIR of Pu²⁴² and of a mixture of Am²⁴³ with Cm²⁴⁴. These feed materials are being produced by long-term irradiation of 10-kg batches of Pu²³⁹ in a Savannah River reactor. The irradiated Pu²³⁹ will be processed at Savannah River to recover the Pu²⁴² as decontaminated PuO₂, and the americium-curium as a solution containing about 3 kg of rare earth fission products. The rare earths will be removed from the americium-curium and the actinide oxides fabricated into HFIR targets in the TRU Facility. Also in the TRU Facility the irradiated HFIR targets will be processed to recover the heavy elements for research uses, and the recovered curium isotopes will be refabricated into HFIR targets.

Progress reports are included on the development of separation processes for the transuranium elements, process equipment development, HFIR target fabrication development, design of the TRU Processing Plant, corrosion studies, and analytical research and development. This work was performed by the Chemical Technology, Metals and Ceramics, Plant and Equipment, Analytical Chemistry, and Reactor Chemistry Divisions of Oak Ridge National Laboratory, and the General Engineering Department of the Oak Ridge Gaseous Diffusion Plant.

Previous reports in this series are:

1. For period ending February 28, 1962 - ORNL-3290.
2. For period ending August 31, 1962 - ORNL-3375.
3. For period ending November 30, 1962 - ORNL-3408.
4. For period ending February 28, 1963 - ORNL-3482.

3. DEVELOPMENT OF CHEMICAL FLOWSHEETS FOR THE OVERALL PROCESS ^{ST only → [Tramex]}

K. B. Brown R. E. Leuze

3.1 Tramex Process Development

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In the Tramex process, the separation of actinide and lanthanide elements is achieved by extraction of the actinides into tertiary amines from concentrated lithium chloride solutions at low acidities. Process conditions were previously determined, and extensive tests have been made in laboratory mixer-settler runs. Development studies reported here were directed toward further improvement and testing of the Tramex Process and included process demonstration at high Cm^{242} levels; use of selected reducing agents to control acid loss in Tramex feed by radiolysis; studies of the effect of small amounts of nitrate on americium and europium extraction behavior; purification of the Alamine 336 extractant by removal of primary and secondary amines; aluminum chloride solubility in Tramex

^aSummer student.

feed; preparation and stability of Alamine 336·HNO₂, which is required for effectively scrubbing ruthenium from strip product; and laboratory demonstration of a method for converting Tramex product from a chloride to a nitrate solution.

3.1.1 Tramex Flowsheet at High Power Density

A series of five batch countercurrent solvent extraction tests of the Tramex flowsheet were made with Cm²⁴² power densities varying from 5 to 10 w/liter. No adverse effect on solvent extraction was noted due to the alpha radiation. However, acid in properly adjusted Tramex feed was destroyed by radiolysis, causing precipitation usually within 28 to 40 hr. These runs were made to explore the effects of various operating conditions; consequently, no one run was made under optimum conditions to obtain both high recovery of curium and high decontamination from fission products. However, the results indicate that the Tramex process is capable of meeting these goals. The best curium recovery observed (measured by raffinate losses) was 99.93%. The best fission product decontamination was 19 for Ce¹⁴¹, 310 for Ru¹⁰³, and 3×10^4 for Zr-Nb⁹⁵.

Description of the Process. -- The Tramex flowsheet was modified for this test as shown in Fig. 1. Feeds were prepared from four targets of Am²⁴¹ oxide in aluminum which had been irradiated for 30 to 60 days in the Oak Ridge Reactor and cooled four to six months. At the time of processing, the targets contained 10 to 20 mg of Cm²⁴². Before chemical processing, the aluminum jackets of the targets were removed mechanically, leaving a compacted aluminum-ameridium oxide pellet about 1/4 in. in diameter, 1/2 in. long, and weighing about a gram. The aluminum matrix was dissolved in 2 M HCl. Dissolution of the metal oxides was ensured by increasing the acid concentration to 6 M and heating the solution at 90°C for about 2 hr. A black, insoluble residue remained; however, this was presumed to be particles of carbon resulting from degradation of die lubricant used during pellet pressing. Solvent extraction feed was prepared by adding about 200 ml of 11 M LiCl to the dissolver solution and evaporating off excess hydrochloric acid. A final temperature of 133°C resulted in acceptable feed, both in terms of salt concentration (10 M LiCl, 0.17 M AlCl₃) and acidity (probably less than 0.08 M HCl).

Fig. 1. Flowsheet for High-Level Tramex Test.

The adjusted feed was contacted with 0.6 M Alamine 336·HCl in diethylbenzene in a semiautomatic, batch, countercurrent solvent extraction apparatus. Volumes were 6, 4.5, and 9 ml per cycle for feed, scrub, and solvent, respectively. The scrub solution was 10.8 M LiCl, 0.02 M HCl containing 500 ppm of a surfactant FX-170¹ to promote phase separation. Curium was stripped from the solvent with 6 to 8 M HCl. Stripped product was washed with a fresh stream of solvent containing either Alamine 336·HNO₂, Alamine 336·HCl, or both of these salts in diethylbenzene. Volumes of strip and wash were each 6 ml per cycle. The apparatus consisted of 6 extraction, 4 scrubbing, 2 stripping, and 8 washing stages. The product was collected in a vessel from which it could be returned to the dissolver in order to enrich the feed in succeeding runs. In this manner five runs were made from the material in the four targets.

Description of Equipment. -- A batch countercurrent solvent extraction apparatus mounted in an alpha-tight enclosure was designed and built for this series of runs. The block diagram in Fig. 2 shows the principal features of the apparatus; these include a dissolver-evaporator, ten mixing-settling chambers, 30 inter-stage transfer chambers with glass ball check valves, six feed chambers, a product collection vessel, 31 sampling points, a waste disposal manifold, a condenser, and an off-gas treatment system.

The ten mixing and settling chambers were equivalent to 20 stages of two-phase contact, because aqueous and organic phases were transferred alternately between mixing cycles. While transferring aqueous phases, it was necessary to draw the organic layers up into storage reservoirs and to return them to the same mixing chamber after the aqueous transfers were complete. Solution transfers were accomplished with pressure or vacuum supplied by a small blower which recirculates air to and from the alpha containment enclosure. Vacuum and pressure were regulated by venting through two 24-in. columns of water. Solutions of either phase were transferred to and from all stages simultaneously. The phases were mixed one

¹FX-170 is nonionic fluorochemical surfactant manufactured by the Minnesota Mining and Manufacturing Company.

Fig. 2. Block Diagram of Apparatus.

stage at a time by vortex mixers controlled individually from the operating area. Sampling was accomplished by impaling evacuated, rubber-diaphragm sample bottles upon tantalum tubes, which were connected to the various sample points. The product collection vessel was identical in construction to the dissolver, and in emergencies it could serve as the hot feed vessel. All the feed vessels were equipped with small metering cups from which measured amounts of feed, scrub, solvent, and strip were withdrawn for each cycle. The cups were refilled by airlifts. The volume of feeds introduced per cycle and the interfaces in the mixing-settling vessels were controlled by proper setting of the heights of the lower ends of the section tubes leading to the transfer chambers. This adjustment had to be made manually before the equipment was placed in the shielded cell. The entire apparatus was surrounded by an alpha containment enclosure and installed in a cell in Building 3019 High Radiation Level Analytical Facility. Operations were accomplished by using masterslave manipulators to turn extension handles on the outside of the alpha enclosure. Fig. 3 is an overall view of the apparatus showing the compact arrangement of the equipment.

Operating Experience. -- The equipment operated very well through most of the runs, although there were some minor difficulties (e.g., in run Cm-3 the stirring magnet was partially dissolved because of a crack in the glass cover). The first radiation-damage failure came at the end of the fourth run after about 30 days of hot operation when the Teflon three-way stopcock in the feed airlift line became sufficiently degraded so that feed could no longer be airlifted through it. In order to make the fifth run, the product collection vessel was used as a feed vessel, and the product was removed from the last solvent extraction stage directly into sample bottles. Alpha radiation, even at 10 w/liter, had no apparent effect on solvent extraction or phase separation. The solutions were thoroughly degassed during the mixing cycle, and there was insufficient time to build up troublesome bubbles of radiolysis gas in the 2 to 5 min allowed for coalescence. Phase coalescence and separation was equally good with either nonradioactive or radioactive feed, but since it was not possible to make perfect separations with a simple dip line, the choice was to entrain a small amount of solvent with the aqueous phase. In the scrubbing, stripping, and washing sections,

Fig. 3. Overall View of Apparatus.

this entrainment was about 0.5 ml per transfer. In the extraction stage solvent entrainment was about 2 ml per transfer.

Run Cm-3 was an exception in that phase separation was poor. Partial dissolution of the stirring magnet resulted in large quantities of iron, nickel, cobalt, and copper in the feed. These elements extracted into the solvent, raising its density considerably. This, coupled with the very high interfacial tension in lithium chloride systems, resulted in very poor phase separation. Several times during an attempt to transfer organic phase the aqueous layer was sucked out from under the organic phase, thus leaving the organic phase behind.

Operating Conditions and Results. -- The five different runs made gave an opportunity to experiment with run conditions such as mixing time, acid strength in the strip, wash composition, etc. Conditions for each of the runs are summarized in Table 3.1. In order to improve phase coalescence at room temperature, 500 ppm of FX-170 was added to the scrub. Run results are shown in Tables 3.2 and 3.3. The main conclusions are as follows:

1. Curium power density in the range 5 to 10 w/liter had no appreciable effect on the mechanical operation of the extraction process.
2. Feed acidity must be kept sufficiently low or curium will reflux in the extraction contactors. Refluxing occurred in runs Cm-2 and Cm-6; as a result, curium recovery was poor.
3. Hydrazine monohydrochloride added to Tramex feed prevents the precipitation of metal hydroxides, but it raises the acidity to an unacceptably high value.
4. Cerium decontamination factors were poor in all runs. This indicates that scrubbing contacts at 25°C for times of about 10 to 60 sec are not adequate to reach equilibrium. The best cerium decontamination factors demonstrated were in runs Cm-2 and Cm-6, in which high feed acidity also caused poor curium recovery. Even though these runs did not demonstrate adequate cerium decontamination, indications are that at proper conditions the Tramex process will effectively remove cerium and rare earths since

Table 3.1 Run Conditions for High-Level Tramex Tests

Run No.	Cm Power Density (w/liter)	Feed Acidity ^a (N)	Agitation Time ^b (sec)	Flow Ratios F/S/E/Str/Wash	HCl Conc. in Stripping Solution (M)	Wash Compound Dissolved in Diethylbenzene
Cm-2	5.0	0.15	10	1/0.75/1.5/1/1	6.0	0.6 M Alamine 336·HNO ₂
Cm-3	6.5	0.05	10	1/0.75/3.0/1/2	6.0	~ 0.3 M Alamine 336·HNO ₂ 0.3 M Alamine 336·HCl
Cm-4	7.2	0.05	10	1/0.75/1.5/1/1	7.0	0.6 M Alamine 336·HNO ₂
Cm-5	8.6	0.05	10	1/0.75/1.5/1/1	8.0	0.6 M Alamine 336·HNO ₂
Cm-6	10.2	0.10 ^c	60	1/0.75/1.5/1/1	8.0	0.1 M Alamine 336·HNO ₂ 0.5 M Alamine 336·HCl

^aThe feed acidity was not measured directly. Indirect evidence indicates the general order of the numbers listed.

^bThe agitation time is of greatest importance in the scrubbing stages. All other stages are thought to reach equilibrium in a few seconds.

^cThis higher acid results from adding hydrazine monohydrochloride to protect against radiolysis.

Table 3.2 Overall Results of High-Level Tramex Tests

Run	Curium Behavior		Decontamination Factors		
	Recovery ^a (%)	Raffinate Loss (%)	Cerium	Ruthenium	Zirconium
Cm-2	5.7	8.4	16	- ^c	3 ^b
Cm-3	67	7.1	5	130	330
Cm-4	112	0.07	6	215	27
Cm-5	128	0.27	7	310	400
Cm-6	4.8	22	19	230 ^b	$> 3 \times 10^4$ ^b

^a Measured by the average aqueous phase concentration in solvent wash stages.

^b Assumes 100% curium recovery since increasing curium extraction would not affect total contaminant in product.

^c Ruthenium contamination was not detectable because of high zirconium content of the product.

Table 3.3 Extractability of Ruthenium and Zirconium from Tramex Feeds

Run	Ruthenium Extracted ^a (%)	Zirconium Extracted ^a (%)
Cm-2	99	99
Cm-3	76	5
Cm-4	92	65
Cm-5	82	24
Cm-6	90	98

^aDetermined by raffinate losses.

previous results from mixer-settler runs made at elevated temperatures demonstrated rare earth decontamination factors greater than 10^4 .

5. Ruthenium decontamination factors were also poor, even though nitrite was added to the wash solvent to improve decontamination. It is probable that the nitrite decomposed during the long residence time in the equipment and thus was not completely effective. Evidence from previous tests indicate that freshly prepared Alamine 336·HNO₂ effectively holds ruthenium in an extractable form.

6. Zirconium decontamination was excellent when the proper process conditions were used. These conditions, which include an 8 M HCl stripping solution and sufficient amine hydrochloride salt in the solvent wash, were used in run Cm-6, and the resulting zirconium decontamination factor was greater than 3×10^4 . Note that in run Cm-5 the zirconium decontamination factor was only 400 even though the stripping solution was 8 M HCl. This lower decontamination resulted from an insufficiency of Alamine 336·HCl in the solvent wash.

7. Zirconium is nearly inextractable from Tramex feed at certain conditions (see Table 3.3). This is presumably due to partial hydrolysis in feed at low acidity. Even though most of the zirconium was extracted in run Cm-6, the overall zirconium decontamination was excellent because of proper stripping conditions.

8. Although none of these runs demonstrated both high recovery of curium and high decontamination from fission products, the overall results of these and previous tests indicate that the Tramex process is capable of meeting these goals.

3.1.2 Control of Acidity in High-Activity-Level Tramex Feed

Since separations by the Tramex process are greatly affected by small changes in acidity, methods are being developed for controlling the acid losses caused by radiolysis. The exact mechanism of the loss is not understood, but there are indications that chloride oxidation is associated with it. Analysis of radiolytic gas from 10 M LiCl containing Cm²⁴² (14 w/liter) gave H₂, O₂, and Cl₂ ratios of 7.3:1.2:1.0, respectively,

but a material balance of the gaseous products did not account for all of the chloride lost by the destruction of the hydrochloric acid. Similarly, an oxygen material balance did not account for sufficient oxygen when the radiolysis of water is assumed to produce $H_2 + 1/2 O_2$; therefore, it appears that some of the oxygen and chlorine produced by radiolysis remain in solution. Further evidence of chlorine and oxygen retention in the solution was demonstrated during acidification of a solution that had become basic as a result of radiolysis. During acid addition, a large quantity of gas was evolved. It consisted of nearly equal quantities of Cl_2 and O_2 , but no H_2 .

Since acid loss appears to result from the oxidation of the chloride ions, the addition of reducing agents to high-activity-level Tramex feed was investigated as a means of keeping the acid within the required concentration range of 0.01 to 0.10 M; it was found that certain reducing agents are effective.

Investigations were made to determine if hydrazine monohydrochloride, formaldehyde, or methanol added to high-activity-level Tramex feed would stabilize the acid at a concentration in the 0.01 to 0.1 N range; the results are shown in Fig. 4. When no reducing agent was present in high-activity-level Tramex feed, the G value for H^+ destruction was about 1.4; however, when $N_2H_4 \cdot HCl$ was present, acid was not destroyed but was produced at this rate. This is equivalent to an acid increase of about 0.1 mole liter⁻¹ day⁻¹ for a Cm^{242} concentration equivalent to 10 w/liter. Presumably the hydrazine reacts to convert chlorine in radiolysis products to HCl and at the same time releases HCl chemically bound in the $N_2H_4 \cdot HCl$ salt.

When 1 vol % formaldehyde was present in 10 M $LiCl$ containing 8 w of Cm^{242} per liter, the H^+ increased from 0.10 M to 0.22 M in ten days. During the next 15 days, the acid concentration decreased from 0.22 M to 0.006 M. The next day the solution became acid deficient, and curium hydroxide precipitated. It is possible to adjust conditions of the Tramex process to operate satisfactorily with feed that is 0.22 M in H^+ ; however, lower acid concentrations are desirable. Additional experiments are

Fig. 4. Effect of Curium-242 Alpha Activity on Acid in 10 M LiCl.

required to determine if larger amounts of formaldehyde can be used to stabilize feed for longer periods of time without causing acid concentrations to exceed 0.22 M.

Methanol was even more effective for maintaining the correct acidity. When 10 vol % methanol was present in 10 M LiCl containing 18 w of Cm^{242} per liter, the solution was stable even after 25 days, and the acid concentration was 0.03 to 0.06 M during the entire 25 days. The accumulated radiation dose was greater than 10 kwh/liter. Additional studies of this method for controlling acidity are in progress. The effect of methanol on the Tramex extraction process must also be determined.

3.1.3 Acid Adjustment in Tramex Feed by Adding Hydrogen Chloride Gas

The equilibration of Tramex feed with hydrogen chloride gas has also been investigated as a means of restoring acidity lost through radiolysis. An equilibrium acid concentration of 1.0 M HCl was obtained when hydrogen chloride gas was bubbled through 10 M LiCl at 25°C. The equilibrium acid concentration was reduced to 0.4 M by increasing the temperature of the LiCl solution to 120°C. Since the acid concentration of Tramex feed should be maintained below 0.1 M, the possibility of equilibrating Tramex feed with inert gas containing a reduced partial pressure of hydrogen chloride was investigated.

Initial experiments established that the partial pressure of hydrogen chloride over 10 M LiCl-0.1 M HCl at 23°C is only 0.45 mm of Hg. This means that the partial pressure of hydrogen chloride in the gas stream must be only 0.45 mm of Hg and that the gas flow necessary to replace acid losses in Tramex feed would be excessive at room temperature. However, by increasing the temperature of the feed, a larger partial pressure of hydrogen chloride can be used, and thus a smaller total gas flow is needed. The effects of increased temperature were investigated by determining equilibrium acid concentrations for 10 and 11 M LiCl solutions contacted with dry helium gas which contained hydrogen chloride at a partial pressure of 23.5 mm. These results are given below:

Temperature of LiCl Solution (°C)	Equilibrium Acid Concentration (M)	
	10 M LiCl	11 M LiCl
70	0.31	0.185
100	0.20	0.11
120	0.14	0.08

The effect of decreasing the partial pressure of hydrogen chloride in a dry helium gas stream equilibrated with 10 M LiCl at 100°C was also investigated. Acid concentrations of 0.199, 0.168, and 0.148 M were obtained at hydrogen chloride partial pressures of 23.5, 9.0, and 2.5 mm of Hg, respectively.

These results indicate that Tramex feed acid could be maintained at about 0.1 M HCl with a gas flow rate of 3 liters per minute per 50 liters of feed when the feed is maintained at 120°C. However, the difficulties attendant with maintaining feed at this temperature are sufficiently severe to make this method of acid control much less attractive than acid control by methanol addition.

3.1.4 Effect of Nitrate on Extraction in the Tramex Process

The addition of small amounts of Alamine 336·HNO₃ to Alamine 336·HCl-DEB was investigated as a possible means of increasing actinide distribution coefficients. (DEB is diethylbenzene.) With higher distribution coefficients, it was thought that control of Tramex feed acid concentrations may be less critical. Unfortunately, acid control is even more critical in the presence of nitrate.

Distribution coefficients were determined for americium, europium, and hydrochloric acid between (a) 11 M LiCl containing 0.05 to 0.20 M HCl and (b) the mixed nitric and hydrochloric acid salts of 0.6 M Alamine 336 in DEB. The concentration of Alamine 336·HNO₃ was varied from 0.01 M to 0.10 M. The results are shown in Fig. 5. Distribution coefficients are plotted against the concentration of Alamine 336·HNO₃ for each feed acid concentration used. Americium and europium distribution coefficients are both increased by the addition of nitrate; however, separation factors between americium and europium are decreased.

Fig. 5. Europium and Americium Distribution Coefficients Between Mixed HNO_3 and HCl Salts of 0.6 M Alamine-336 in Diethylbenzene (DEB) and 11 M LiCl Containing 0.05 to 0.20 M HCl as a Function of Extractant Composition.

The distribution coefficients of hydrochloric acid in the mixed chloride-nitrate systems tested were found to be identical to the hydrochloric acid distribution coefficients in the all-chloride system. Americium and europium distribution coefficients can therefore be compared as a function of the concentration of hydrochloric acid in the organic phase for various nitrate concentrations (Fig. 6). These curves emphasize decreasing separation factors with increasing nitrate concentration and demonstrate an americium-europium separation factor dependence on the concentration of free acid. Since separation factors are not affected by free acid concentration in the all-chloride system, the mixed chloride-nitrate system appears to be more sensitive to free acid than the all-chloride system even though the distribution coefficients are greater.

3.1.5 Purification of Alamine 336

Alamine 336 is a mixture of octyl and decyl tertiary amines, but small amounts of primary and secondary amines are also present. Only the tertiary amine hydrochlorides extract actinides from concentrated lithium chloride solutions. Primary and secondary amines appear to reduce actinide distribution coefficients somewhat; and because they have a high viscosity, their presence needlessly increases the viscosity of the Tramex extractant. It is desirable, therefore, to separate the tertiary amine from the others. Since the amine hydrochloride salts are not soluble in raw amine, partial neutralization produces two solvent phases. This method was used to fractionate a sample of Alamine 336 into a bottom layer containing 10 mole % of the amines (mostly primary and secondary) and a top layer of partially purified tertiary amine. Each cut was dissolved in diethylbenzene to a concentration of 0.6 M total amine hydrochloride, and americium extraction from 10 M LiCl--0.15 M AlCl₃ at various concentrations of hydrochloric acid was determined. The variation in distribution coefficients for treated and untreated Alamine 336·HCl as a function of the concentration of hydrochloric acid in the organic phase is shown in Fig. 7. These results indicate that by simply neutralizing with hydrochloric acid and discarding 10% of the Alamine 336, most of the primary and secondary amines can be removed, producing a purified Alamine 336 that gives americium distribution coefficients that are about 50% higher.

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Fig. 6. Europium and Americium Distribution Coefficients Between Mixed HNO_3 and HCl Salts of 0.6 M Alamine-336 in Diethylbenzene (DEB) and 11 M LiCl as a Function of Extractant Acidity.

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Fig. 7. Effect of Primary and Secondary Amine Removal from Alamine-336 on Americium Distribution Coefficients.

3.1.6 Europium Distribution Coefficients in the Tramex Process

Recent determinations of europium distribution coefficients between 0.6 M Alamine 336-DEB and 11 M LiCl at various concentrations of hydrochloric acid indicate that previously reported europium values are high.² A comparison between the two sets of data are shown in Fig. 8. The reason for the discrepancy between these two sets of data is not understood; however, it does serve to emphasize the decisiveness of process variables in the Tramex system.

3.1.7 Solubility of AlCl_3 in LiCl-HCl Mixtures

As previously reported,³ the maximum solubility of aluminum chloride in 10 M LiCl is 0.2 M. At these salt concentrations hydrochloric acid in excess of 0.05 M will precipitate aluminum chloride. The solubility of aluminum chloride in 10 M LiCl solution decreases as the acid concentration increases (Fig. 9). At acid concentrations of 0.45 and 0.90 M, the solubilities are 0.15 and 0.10 M, respectively.

3.1.8 Stability of Alamine 336· HNO_2

In the Tramex process Ru^{4+} extracts into the organic phase; however, after extraction it is slowly reduced by the amine solvent to inextractable Ru^{3+} . One proposed method of maintaining ruthenium in its extractable form during curium stripping operations is to incorporate Alamine 336· HNO_2 into the organic scrubbing section of the strip column. The preparation and stability of 0.6 M Alamine 336· HNO_2 -DEB was therefore investigated.

Alamine 336· HNO_2 can be readily prepared by contacting 0.6 M Alamine 336·HCl-DEB with 1 M KNO_2 ; however, this amine salt decomposes upon standing at room temperature. In 72 hr, about 50% of the nitrous acid was destroyed (Fig. 10). When the amine salt was kept in contact with 8 M HCl,

²R. E. Leuze et al., Transuranium Quart. Progr. Rept. Feb. 28, 1963, ORNL-3482, p 14.

³R. E. Leuze et al., Transuranium Quart. Progr. Rept. Nov. 30, 1962, ORNL-3408, pp 21-22.

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Fig. 8. Europium Distribution Coefficients Between 0.6 M Alamine-336·HCl in Diethylbenzene (DEB) and 11 M LiCl as a Function of Extractant Acidity.

Fig. 9. Solubility of AlCl_3 in Concentrated LiCl Solution Containing HCl .

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Fig. 10. Decomposition of 0.6 M Alamine-336· HNO_2 in Diethylbenzene (DEB) at 25°C.

only 20% of the nitrous acid remained after 72 hr. Contacting the amine salt with 8 M HCl at 60°C further increased the decomposition rate. At 60°C the concentration of nitrous acid was decreased from 0.6 to 0.1 in 30 min, and the nitrous acid was totally destroyed in 4 hr.

3.1.9 Laboratory Demonstration of Chloride-to-Nitrate Conversion for Curium-242 Product

Curium-242 product from the Tramex process will be contained in about 12 liters of 8 M HCl. The proposed method of converting this to a nitrate solution is to evaporate to 4 liters, add 4 liters of concentrated nitric acid, and evaporate to 4 liters. This process is to be repeated two more times.

This conversion was tested at 1/10 scale in tantalum equipment with simulated feed containing mixed rare earths as substitutes for americium and curium.

Chloride concentration of the product was reduced to 1 or 2 ppm after the second boiloff of the nitric acid. The final product was approximately 15 M HNO₃ and contained 0.5 g of rare earths per liter. Noncondensable acid reaction products (probably nitrosyl chloride) were readily scrubbed from the off-gas with dilute caustic. From all three boildowns, a total of 5.5 equivalents of acid per liter of product were collected in the caustic trap.

Some ruthenium decontamination can be obtained if RuO₄ is volatilized during this conversion. Ruthenium added as the trichloride does not volatilize even from boiling concentrated nitric acid during the final stages of conversion. Sodium bismuthate in concentrated nitric, or ozone bubbled through concentrated nitric containing sodium nitrite, effectively oxidized ruthenium to the volatile RuO₄ when the solutions were boiled.

Ruthenium decontamination factors of 70 to 100 were obtained with NaBiO₃ concentrations as low as 0.004 M, and a ruthenium decontamination factor of 5 was obtained with ozone in the presence of 0.02 M NaNO₂.

3.2 Ion Exchange Process Development

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Although most of the transuranium element processing will be based on solvent extraction, ion exchange methods are invaluable for some separations. Important applications include Am-Cm and Cf-Es-Fm separation by chromatographic elution, and small-scale purifications which can be done in simple equipment. Work reported here includes americium-curium separations at high alpha-activity levels, laboratory-scale separation of americium-241 from rare earths, and isolation of an $\text{Am}^{241}\text{-Cm}^{242}$ product from fission products and aluminum.

3.2.1 Separation of Curium from Americium at High Activity Levels

Separation of curium from americium by chromatographic elution from a spring-loaded cation exchange column with ammonium α -hydroxyisobutyrate at activity levels of 50 w/liter was achieved. Two milligrams of Cm^{242} and 4 mg Am^{241} were loaded on a 20-ml column of Dowex 1-X3 (-400 mesh) resin at 80°C. The curium and americium were eluted with 0.4 M butyrate at pH 4.2 at a flow rate of $0.3 \text{ ml cm}^{-2} \text{ min}^{-1}$. Gassing problems were controlled, and separation of the bed was prevented by spring-loading the column of resin. Ninety percent of the curium and americium were recovered, with 10% cross contamination.

The separation of curium from americium was achieved by chromatographic elution from a spring-loaded anion exchange column with lithium nitrate at activity levels of 100 w/liter. The characteristic cherry-red glow from the activity separated into a white band and a red band. The white glow was associated with curium, while the red was presumably due the excitation of americium. The separation factor was 1.87, and results indicate that the separation of curium from americium could be achieved with about 1% cross contamination.

3.2.2 Americium Purification

Nine grams of americium have been separated from contaminant rare earths by LiCl anion exchange. Six runs were required with a glass column 1 in. in diameter and 45 cm long; packed with 100- to 200-mesh Dowex 1-X10

resin. All flow rates were $1 \text{ ml cm}^{-2} \text{ min}^{-1}$, and column temperature was maintained at 84°C . Nearly 2 g of americium could be readily loaded on the top quarter of the resin bed from eight column-displacement volumes of $12 \text{ M LiCl--}0.1 \text{ M HCl}$ feed. Six column volumes of $10 \text{ M LiCl--}0.1 \text{ M HCl}$ wash was used to remove rare earths; however, no rare earths were detectable by spectrographic analysis after four column volumes of wash. Product americium was eluted with 0.5 M HCl at concentrations of 10 to 15 g/liter. The purified americium will be used in HFIR target preparation and dissolution studies.

3.2.3 Anion Exchange Processing of 20 mg Curium-242

An irradiated Am^{241} target containing 22 mg of Cm^{242} was processed in Building 3019 Analytical Hot Cells by the LiCl-anion exchange method. The decontaminated product, which contained both Am^{241} and Cm^{242} , was used to determine the effects of alpha radiation on Tramex solutions.

The aluminum target, which "read" greater than 1000 r/hr, was dissolved in $4.2 \text{ M NaOH--}3.4 \text{ M NaNO}_3$. After filtering and washing, the residue was dissolved in 5 ml of 12 M HCl . Fifty milliliters of 13.4 M LiCl was then added to yield a solution 12.5 M in LiCl and 0.5 M in HCl as feed for the anion exchange column. The column, packed with 125 ml of Dowex 1-X8 (100 to 200 mesh) resin was 20 cm long and 6 cm^2 in cross sectional area. The temperature was maintained at 80°C . Feed was loaded at a flow rate of $0.5 \text{ ml cm}^{-2} \text{ min}^{-1}$. The column was washed with 100 ml of $12.5 \text{ M LiCl--}0.5 \text{ M HCl}$ solution. Rare earths were eluted with ten column volumes of $10.5 \text{ M LiCl--}0.5 \text{ M HCl}$; however, almost complete rare earth removal was obtained in four column volumes. Americium and curium were stripped from the resin with four column volumes of $6 \text{ M LiCl--}0.5 \text{ M HCl}$.

Nearly complete decontamination was obtained from all fission product activity except ruthenium. Ruthenium-103 and -106 activity was about equal to 30% of the Cm^{242} gamma activity. The gross fission product decontamination factor was about 10^4 .

The residual resin contained all the Zr^{95} and some $\text{Ru}^{103-106}$. The Zr^{95} was eluted with 0.1 M HCl ; however, ruthenium would not strip and was discarded with the resin.

3.3 Chemical Process Development for Making Oxides to be Used in HFIR Targets

Methods of preparing actinide oxides for use in HFIR targets must be developed. So far, work has been limited to the preparation of Pu^{239} dioxide for use in HFIR target prototypes. This development and a method of recovering PuO_2 from target rejects is reported here.

3.3.1 Preparation of PuO_2 for HFIR Target Prototypes

Seventy-nine grams of high fired PuO_2 containing 69.27 g of Pu^{239} was prepared for use in prototype HFIR targets. Particle size of the fired oxide was as follows:

<u>Screen Size</u>	<u>Wt %</u>
-70 + 140	48.37
-140 + 170	15.89
-170 + 200	9.74
-200 + 325	26.00

This material will be mixed with aluminum powder and pressed into pellets. Fine-particle PuO_2 (-325 mesh) must be avoided to ensure a continuous aluminum phase in the pressed pellet.

One method of preparing +325-mesh PuO_2 was reported in the February quarterly report.⁴ In this procedure $\text{Pu}(\text{NO}_3)_4$ was precipitated with NH_4OH . The precipitate was washed, dried at 150°C , and fired at 1200°C . Either the fired oxide or the dried hydroxide can be ground to the desired particle size range. However, during grinding, sizable quantities of -325-mesh particles are generated and must be recycled. The recycle procedure consisted in plutonium dissolution by refluxing for several hours in concentrated nitric acid; during which time, 2 M HF was slowly added until a concentration of 0.01 M HF was reached. After dissolution, the plutonium was adjusted to the plus four valence and then reprecipitated with NH_4OH .

⁴R. E. Leuze et al., Transuranium Quart. Progr. Rept. Feb. 28, 1963, ORNL-3482, pp 31-33.

Since high-fired PuO_2 and dried $\text{Pu}(\text{OH})_4$ are very difficult to dissolve, a sol-gel PuO_2 preparation was investigated. If a plutonium sol can be prepared, it would be possible to evaporate the sol to dryness and grind the resultant gel to the desired particle size. Fine particles generated during grinding could be readily resuspended as a sol in water, and plutonium dissolution and valence adjustment would not be necessary. A possible procedure for preparing plutonium sol was first investigated with thorium. A satisfactory sol was prepared from $\text{Th}(\text{NO}_3)_4$ by hydroxide precipitation. This method consists in precipitating $\text{Th}(\text{OH})_4$ from 0.5 M $\text{Th}(\text{NO}_3)_4$ solution with excess NH_4OH . The precipitate is washed with water until the pH of the supernatant is about 8.0. The hydroxide is then dried and slowly heated to 300°C . This material is readily dispersed in water to form a sol, which can be dried, ground, screened, and fired to produce thoria particles of the desired size. The pH of the sol is 3.2, and the dried sol can be readily resuspended as a sol by water.

The above procedure was used in an attempt to prepare a plutonium sol from $\text{Pu}(\text{NO}_3)_4$. However, $\text{Pu}(\text{OH})_4$ which was heated to 300°C could not be redispersed in water. Attempts to make a sol by starting with $\text{Pu}(\text{OH})_4$ dried at 150°C were also unsuccessful even though digestion times were as much as 7 hr at 80°C and the pH was varied from 0.5 to 3.0.

What appeared to be a plutonium sol was prepared, however, by the following method. Plutonium hydroxide, made by NH_4OH precipitation, was washed until the pH of the supernatant was 8.5. The hydroxide was slurried in water and digested at 80°C , while the pH was gradually reduced to 1.8 by nitric acid. After 18 hr of digestion, 90% of the $\text{Pu}(\text{OH})_4$ was dispersed. Presumably, a sol had formed since none of the suspended plutonium settled in 16 hr. After drying, the resultant solid was readily dispersible in water. The pH of the redispersed sol was 2.0. The sol was dried, ground, screened, and fired at 1200°C . Although the appearance of the fired oxide was good, further tests will be necessary to determine whether the density and strength of this material is satisfactory for making targets.

3.3.2 Dissolution of Prototype HFIR Targets

Four unirradiated prototype HFIR targets were processed for plutonium recovery. About 60 g of plutonium was recovered in all. These targets consisted of a packed mixture of high-fired PuO_2 and aluminum powder. The aluminum was readily dissolved in a solution 1.2 M in NaOH and 1.5 M in NaNO_3 . One liter of dissolver solution was used per mole of aluminum. Plutonium losses during aluminum dissolution averaged 0.7 mg/liter (0.005%). The PuO_2 was washed with hot 2 M HNO_3 for additional decontamination from aluminum, and similar plutonium losses were incurred. The PuO_2 was dissolved by refluxing for long times in concentrated nitric acid. During reflux, 2 M HF was slowly added until a concentration of 0.01 M was reached. The plutonium product, concentrated to 24 g of plutonium per liter by evaporation, contained 0.02 g of aluminum per liter of solution.

The dissolution of aluminum in 2 M HCl was also tested; however, plutonium losses were increased from 0.005% to 0.1%. Plutonium oxide could not be dissolved in either 6 or 12 M HCl ; less than 0.2% had dissolved after refluxing for more than 24 hr.

Dissolution in caustic appears to be useful for recovering plutonium from HFIR target rejects that are not satisfactory for irradiation. It may not be necessary to dissolve and then re-form the plutonium oxide following aluminum dissolution if the oxide is thoroughly washed.

3.4 Alternative Extraction Method for Separating Lanthanides from Trivalent Actinides

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A new extraction method for separating the trivalent actinides from the lanthanides was found and is being studied as a possible alternative to the Tramex process. The new method has potential advantages over the Tramex process in that it does not require the use of corrosive chloride solutions nor close control of the concentrations of aqueous components. Moreover, separations are not affected by the presence of

large concentrations of nitrate ion in the aqueous phase. Equipment being obtained for the Transuranium Processing Plant was designed for the Tramex process but will be suitable for this system if additional development work demonstrates significant advantages for the new method.

3.4.1 Method

The method consists in extracting the lanthanides and yttrium away from the actinides by contacting a mixed carboxylic acid-aminopolyacetic acid solution of these elements with a dialkylphosphoric acid or an alkylalkyl- or alkylarylphosphonic acid in an aromatic diluent. Americium, curium, and other trivalent actinides left in the aqueous solution may be recovered by precipitating them as oxalates. The actinide elements may also be recovered in a second solvent extraction cycle by contacting the aqueous raffinate from the group-separation step with a higher concentration of the reagent used to extract the lanthanides or with a stronger extractant. (The amount of reagent in the solvent is an important and useful variable because the extractability of these elements is proportional to nearly the third power of the extractant concentration.) Aliphatic diluents are preferred in the second cycle because the extraction coefficients are higher with aliphatic than with aromatic diluents. Since extractions of the trivalent elements are highly dependent on pH, they are easily stripped from the solvent with dilute nitric acid. Stripping with nitric acid gives a solution suitable for use as a feed to the phosphonate extraction process for the separation of the transcurium elements from americium and curium.

One of the several possible flowsheets is shown in Fig. 11. The extractant in the group-separation step is a dilute solution of di(2-ethylhexyl)phosphoric acid (HDEHP) in diisopropylbenzene (DIPB). The feed is a solution of a mixture of elements in glycolic acid, and the aqueous scrub solution is glycolic acid containing pentasodium diethylenetriaminepentaacetate (Na_5DTPA). The extractant in the second contactor is a more concentrated solution of the stronger extractant, 2-ethylhexyl phenylphosphonic acid ($\text{HEH}[\text{OP}]$) in a more favorable diluent, n-dodecane. There is also a scrub with a small concentration of Na_5DTPA

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Na₅ DTPA - PENTASODIUM DIETHYLENETRIAMINE PENTAACETATE
DIPB - DIISOPROPYLBENZENE
HDEHP - DI(2-ETHYLHEXYL)PHOSPHORIC ACID
HEH[φP] - 2-ETHYLHEXYL PHENYLPHOSPHONIC ACID
Ⓝ - RELATIVE FLOW RATE

Fig. 11. Tentative Flowsheet for Separation of Americium and Curium from Lanthanides.

to aid in decontamination from fission products. In the third contactor the desired elements are stripped from the extractant with dilute nitric acid, which is scrubbed with fresh extractant.

3.4.2 Fundamental Extraction Data

In tests with americium, cerium, and europium, single stage Ce/Am and Eu/Am separation factors were greater than 100 when extracting with diisopropylbenzene solutions of di(2-ethylhexyl)phosphoric acid from aqueous solutions 0.05 to 0.2 M in diethylenetriaminepentaacetic (DTPA) acid and 0.5 to 3 M in any of several carboxylic acids, including glycolic, lactic, tartaric, and citric acids and glycine nitrate. Curium behavior was always very similar to americium behavior. Separation factors were lower when DTPA was replaced by compounds of somewhat similar structure, for example, nitrilotriacetic (NTA), hydroxyethylethylenediaminetriacetic (HEDTA), 1,2-diaminocyclohexanetetraacetic acid (DCTA), and triethylenetetraminehexaacetic (TTHA) acids. Comparative tests could not be made with ethylenediaminetetraacetic (EDTA) acid owing to the low solubility of this compound in the carboxylic acid solutions used.

The effect of varying the concentration of DTPA on extraction and separation is illustrated in Fig. 12. From 0 to 0.05 M, the complexing agent has more effect on americium and the heavier lanthanides than on cerium, so that the separation between the lanthanides and americium is increased while the differences between the lanthanides decrease. Increasing the pH of a solution containing a small concentration of DTPA (0.008 M, Fig. 13) also increases the separation, in agreement with the expected greater effectiveness of this type of complexer at higher pH values.

In another test, Ce/Am separation factors greater than 100 were obtained by extracting from a nitrate solution that was 0.1 M in DTPA (pH 2.5) but did not contain any other carboxylic acid. However, it was found later that this solution was unstable (supersaturated) and also that the extraction rate for europium was very slow. Moreover, the control of pH is much more difficult in the absence of a carboxylic acid.

Fig. 12. Extraction by 0.3 M HDEHP-DIPB from 1 M Glycolic Acid, Na₅ DTPA.

Fig. 13. Extraction by 0.3 M HDEHP-DIPB from 0.5 M Citric Acid, 0.008 M Na_5DTPA .

In tests of relative separation factors obtainable with various extractants, the following order was found: 2-ethylhexyl phenylphosphonic acid > di(2-ethylhexyl)phosphoric acid > 2-ethylhexyl chloromethylphosphonic acid > di(tetramethylbutyl)phenylphosphonate > diphenylphosphoric acid > trioctylphosphine oxide.

In other tests with various carboxylic acid solutions that did not contain auxiliary complexants such as aminopolycarboxylic acids, the extractability of americium relative to the lanthanides varied with the particular carboxylic acid used. For example, in extractions by di(2-ethylhexyl)phosphoric acid from mineral acids, americium is homologous with praseodymium. In the presence of 1 M glycolic acid the relative americium extraction was shifted to give a Ce/Am separation factor of 2. The greatest effect was obtained with diglycolic (oxydiacetic) acid, which at a concentration of 1 M gave a Ce/Am separation factor of 4.

Also, increasing the pH of the aqueous phase increased the Am/Ce factors. For example, the factor of 2 for 1 M glycolic acid at its normal pH of 1.8 was increased to 6.5 by adjusting the aqueous pH to 3.5 with sodium hydroxide. Figure 14 summarizes the relative extractability of americium, cerium, and europium by diisopropylbenzene solutions of di(2-ethylhexyl)phosphoric acid from several types of aqueous solutions. All values in the figure are normalized to give americium extraction a value of 1. The great advantage of using complexants such as DTPA is obvious.

3.4.3 Mixer-Settler Demonstration

A continuous countercurrent test of the method was made, using mixer-settlers. The flowsheet (Fig. 15) followed in this experiment was somewhat different from the example given previously in Fig. 11. The principal changes were the use of HEH[Φ P] diluted with diethylbenzene (DEB) as the solvent, and the use of lactic acid rather than glycolic acid as the aqueous constituent. The feed contained irradiated americium, and the purpose of the experiment was to measure the recovery of curium and its decontamination from lanthanides and other radioactive fission products.

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Fig. 14. Relative Extractabilities of Americium and Lanthanides by Di-(2-ethylhexyl) phosphoric Acid in Diisopropylbenzene from Various Aqueous Solutions.

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Fig. 15. Experimental Flowsheet for Separation of Americium and Curium from Lanthanides and Other Fission Products.

In the first contactor, more than 99% of the lanthanides were extracted along with less than 0.1% of the curium. No other fission product activity was detectable in the extracted lanthanide fraction.

In the second contactor, 80% of the curium was extracted along with traces of Zr^{95} and Ba^{140} . Decontamination from ruthenium was greater than 1000. The poor extraction of curium is believed to be due to a slow rate of extraction from the highly complexing aminopolyacetic acid solution. Further testing will be necessary to determine the mechanism, cause, and cure of this behavior.

In the stripping section, the Zr^{95} was kept in the organic phase by scrubbing the strip solution with additional extractant. The resulting strip product contained only the Ba^{140} , along with the curium.

3.4.4 Reversed-Phase Chromatography

A simple multistage test of the effectiveness of one separation system was made by using the reversed-phase chromatographic procedure. A 20-cm-high wet-packed column contained 5 ml of 0.3 M HDEHP in DIPB absorbed in 5 g of microporous polyethylene granules. A mixture of Ce^{144} and Am^{241} was deposited at the top of the column by extraction from a small volume of water. Elution with a solution 1 M in glycine nitrate and 0.05 M in Na_5DTPA removed all the Am^{241} from the column in less than four column volumes, while all the Ce^{144} remained on the column until it was eluted by 1 N HNO_3 (Fig. 16).

3.4.5 Radiation Damage

In static tests with gamma radiation from a Co^{60} source, and in dynamic tests with Cm^{242} in solution, group separation factors were decreased only very slowly as the DTPA complexing agent was decomposed by radiation (Figs. 17 and 18).

3.4.6 Extraction of Other Elements

Tests were made of the extraction of other cations that might be expected in feed solutions, for example, fission or corrosion products or impurities in reagents. The extractant was 0.3 M HEH[OP] in diethylbenzene. The aqueous solutions were 1 M in lactic acid and

Fig. 16. Separation of Americium and Cerium by Reversed-Phase Chromatography.

Fig. 17. Effect of Gamma Irradiation: 0.3 M HDEHP-DIPB, 1 M Glycolic Acid, 0.025 M $Na_5 DTPA$.

Fig. 18. Effect of Alpha Irradiation: 0.3 M HDEHP-DIPB, 1 M Glycolic Acid, 0.1 M Na_5 DTPA.

contained various concentrations of Na_5DTPA . The results should be considered only a very rough guide to those to be expected from using different concentrations of reagents, or different reagents, in the aqueous and organic phases.

The data (Table 3.4) show that in the system tested, very few elements other than the rare earths were highly extracted from solutions containing Na_5DTPA . However, the behavior of barium, silver, cadmium, chromium, tin, strontium, zirconium, and zinc was such that they may be extractable at some concentrations of Na_5DTPA . The behavior of californium of the trivalent actinide group is discussed below.

3.4.7 Extraction of the Transcurium Elements

The data presented above make it possible to devise a satisfactory flowsheet for separating the lanthanides and yttrium from americium and curium. However, as noted previously, the greater extractability of the heavier actinides creates a more difficult problem in separating these elements from the lanthanides.

Data on the extraction of europium, americium, and californium by organic solutions of HDEHP and $\text{HEH}[\phi\text{P}]$ from various aqueous solutions containing DTPA and some other aminopolyacetic acids are given in Table 3.5. While the Eu/Cf separation factors vary considerably, HDEHP generally gave a larger value. The highest value for a carboxylic acid solution was obtained in extraction by HDEHP in DIPB from a lactic acid-DTPA solution. This system is also suitable for the Eu/Am separation. The Eu/Cf separation factor of 22 seems small only in comparison with Eu/Am separation factors of about 100. A larger Eu/Cf separation factor was obtained with a nitrate solution containing DTPA without a carboxylic acid, but this system is less practicable because of the lack of a buffer. Suitable Eu/Cf separation factors were also obtained with a lactate solution containing DCTA as the complexing agent, but americium was even more extractable than californium in this case. In extractions by $\text{HEH}[\phi\text{P}]$ from solutions containing various carboxylic acids and DTPA, the order of variation of Eu/Cf separation was as follows:

α -hydroxyisobutyric > lactic > formic > citric > glycine nitrate.

Table 3.4 Extraction Behavior of Selected Metal Cations

Organic phase: 0.3 M HEH[OP] in DEB

Aqueous phase:

Lactic Acid, M	=	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Na ₅ DTPA, M	=	-	.01	.025	.50	.10	.25	.50
pH	=	1.85	2.10	2.35	2.65	2.92	3.40	3.85

Metal Ion	Distribution Coefficients ^a						
Am ³⁺	320	53	14	4.3	1.5	0.51	
Cf ³⁺	2310	238	101	53	21	9.7	
Ce ³⁺	630	580	490	340	130	47	
Eu ³⁺	4100	3200	1160	360	122	40	
Ru ³⁺	1.1 ⁻³	2.5 ⁻⁴	2.4 ⁻⁴	2.6 ⁻⁴	4.3 ⁻⁴	2.5 ⁻³	1.6 ⁻³
Zr ⁴⁺	93	0.81	0.44	0.097	0.096	0.094	0.066
Ag ¹⁺	0.10	0.17	0.22	0.36	0.52	0.87	1.0
Ba ²⁺	4.9 ⁻³	4.6 ⁻³	1.2 ⁻²	3.5 ⁻²	0.12	0.36	0.73
Cd ²⁺	8.9 ⁻³	2.6 ⁻²	5.0 ⁻²	0.51	2.5	260	400
Cr ³⁺	1.2 ⁻³	3.5 ⁻³	1.4 ⁻²	5.7 ⁻²	0.16	0.67	1.7
Fe ³⁺	146	2.6	0.74	0.29	3.8 ⁻³	3.8 ⁻³	3.8 ⁻³
Mo ⁶⁺	4.6 ⁻²	2.4 ⁻³	7.9 ⁻³	8.4 ⁻³	2.1 ⁻⁴	2.2 ⁻⁴	6.6 ⁻⁴
Ni ²⁺	2.0 ⁻³	2.0 ⁻³	2.0 ⁻³	2.0 ⁻³	2.0 ⁻³	2.0 ⁻³	2.0 ⁻³
Pd ²⁺	8.3 ⁻⁴	1.3 ⁻³	8.2 ⁻⁴	2.0 ⁻³	8.2 ⁻³	1.4 ⁻³	1.2 ⁻³
Sn ²⁺	63	47	22	7.4	3.0	0.67	0.29
Sr ²⁺	6.7 ⁻³	6.9 ⁻³	2.3 ⁻²	8.0 ⁻²	0.23	0.44	1.5
Zn ²⁺	1.7	2.0	1.9	1.8	2.0	1.8	1.8

^aAn abbreviated notation is used to write the distribution coefficient. For example, 1.1⁻³ stands for 1.1 x 10⁻³.

Table 3.5 Extraction of Europium, Americium, and Californium Under Various Conditions

Aqueous Phase	Organic Phase									
	0.1 M HEH[ϕ P]-DEB					0.3 M HDEHP-DIPB				
	Distribution Coefficients			Separation Factors		Distribution Coefficients			Separation Factors	
	Eu	Am	Cf	$\frac{Eu}{Am}$	$\frac{Eu}{Cf}$	Eu	Am	Cf	$\frac{Eu}{Am}$	$\frac{Eu}{Cf}$
1 M glycolic acid--0.1 M Na ₅ DTPA pH 3.4	4.4	.048	1.3	92	3.1	1.4	.027	.33	52	4.3
1 M citric acid--0.1 M Na ₅ DTPA pH 2.7	74	.82	23	90	3.2					
5 M formic acid--0.1 M Na ₅ DTPA pH 1.68	610	10.7	165	57	3.7					
1 M lactic acid--0.1 M Na ₅ DTPA pH 2.9	13	15	2.1	88	6.2	4.4	.047	.20	93	22
1 M α -hydroxyisobutyric acid--0.1 M Na ₅ DTPA, pH 3.3	5.7	.059	.38	97	15	2.1	.025	.13	84	16
1 M glycine·HNO ₃ --0.1 M Na ₅ DTPA	8.1	1.0	6.9	8	1.2					
1 M NH ₄ NO ₃ --0.1 M Na ₅ DTPA, pH 2.5	22	.22	.62	100	35	9.1	.11	.29	82	31
1 M α -hydroxyisobutyric acid-- 0.1 M Na ₅ DTPA, pH 3.3	5.7	.057	.38	97	15	2.1	.025	.13	84	16
1 M α -hydroxyisobutyric acid-- 0.1 M Na ₃ HEDTA, pH 2.45	240	4	20	60	12					
1 M NH ₄ lactate--0.1 M Na ₄ DCTA, pH 4.0	7.0	.95	.35	7	20	4.1	.24	.20	17	20

The extraction of europium, americium, and californium by HDEHP in DIPB from a 1 M α -hydroxyisobutyric acid solution was tested at various pH values in the range of 3 to 4. The Eu/Cf separation factor was 16 at pH 3 and decreased to 10 at pH 4 (Fig. 19).

In tests with other reagents, diphenylphosphoric acid was found to be an ineffective extractant for process use. With another compound, 2-ethylhexyl chloromethylphosphonic acid, the order of californium and americium extractibility was reversed, but the Eu/Am and Eu/Cf separation factors were only 7 and 12. The addition of tributyl phosphate, trioctylphosphine oxide, and thenoyltrifluoroacetone to HDEHP generally decreased the extraction of europium, americium, and californium.

Other reagent combinations are being studied in search of a system that will afford increased separation of californium and einsteinium from the lanthanides.

3.5 Extraction of Americium(VI)

B. Weaver

The extraction of Am(VI) was studied in comparison with that of Am(III) in a search for differences large enough to be useful in the separation of americium from curium, which is always too similar to Am(III) for easy separation. It was expected that Am(VI) would be relatively highly extractable under conditions that gave high extraction of U(VI) and Pu(VI).

Extractions of Am(VI), prepared by the silver-catalyzed persulfate procedure of Moore,⁵ were compared with extractions of Am(III) from similar aqueous solutions. All work was at tracer-level concentrations. Extractants used were di(2-ethylhexyl)phosphoric acid (HDEHP), tributyl phosphate (TBP), tri-n-octylphosphine oxide (TOPO), and Alamine 336 (a mixed octyl-decyl tertiary amine) nitrate.

Extraction by di(2-ethylhexyl)phosphoric acid in diisopropylbenzene (DIPB) from dilute nitric acid solutions showed a very high preference

⁵F. L. Moore, Anal. Chem. 35, 715 (May 1963).

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Fig. 19. Effect of pH on Europium, Americium, and Californium Extraction Behavior.

for Am(III) rather than the expected and previously reported⁶ high preference for Am(VI) (Table 3.6). Americium(III) was more extractable than Am(VI) by a factor greater than 10^4 from 0.01 N HNO_3 .

Table 3.6 Extraction of Americium(III) and (VI)
by Di(2-ethylhexyl)phosphoric Acid

Organic phase: 0.3 M HDEHP in DIPB

Aqueous Phase	Distribution Coefficient, E_a^0	
	Am(III)	Am(VI)
0.01 <u>N</u> HNO_3	≥ 5000	0.12
0.1 <u>N</u> HNO_3	1.1	0.019
0.1 <u>N</u> LiNO_3	≥ 8000	1.9
1.0 <u>N</u> LiNO_3	≥ 5000	3.3
2.0 <u>N</u> LiNO_3	≥ 1500	2.3

In extractions by undiluted tributyl phosphate (TBP) from nitric acid, Am(III) was about five times as extractable as Am(VI) when the nitric acid concentration was greater than 2 N. Americium(III) was about 30 times as extractable as Am(VI) by 1 M TBP in Amsco 125-82 from 5 N NaNO_3 .

Extraction of Am(VI) by tri-n-octylphosphine oxide in DIPB from slightly acidified lithium nitrate solutions was low and nearly independent of the concentration of LiNO_3 , while extraction of Am(III) reached a maximum when the concentration of LiNO_3 was about 2 N. Am(III) was 200 times as extractable as Am(VI) from a solution 0.1 N in HNO_3 and 2 N in LiNO_3 or 4 N in NaNO_3 .

Americium(VI) was extracted preferentially to Am(III) by 30% Alamine 336 in DIPB from aqueous solutions less than 4 N in LiNO_3 , but increasing the concentration of LiNO_3 to 9 N reversed the preference to a factor

⁶R. A. Penneman and T. K. Keenan, The Radiochemistry of Americium and Curium, NAS-NS-3006 (1960).

of 10 in favor of Am(III). Both species of americium were highly extractable from the concentrated nitrate solution.

Preferential extraction of Cm(III) should be useful in the separation of curium from americium for analytical purposes or wherever the extraction can be performed rapidly enough that the reduction to Am(III) by radiolysis from alpha decay is not too great. It would not be applicable when any large amount of Cm²⁴² is present.

It should be noted that the tests described above were all made at tracer level. While it seems certain that the americium species in solution before extraction was Am(VI), there can be no certainty of the oxidation state in either phase after extraction until tests have been made at sufficiently high concentration that spectrophotometric studies can be made of both the organic and aqueous phases.

(S) → [for Thamel Process]

4. EXPERIMENTAL ENGINEERING STUDIES

P. A. Haas

A. D. Ryon

C. D. Watson

Experimental studies are being carried out as necessary to the engineering design of the chemical processing cells. In addition to development of process equipment components, these include testing in a mockup of procedures and equipment for use in the cell cubicles and testing of the irradiation stability of protective coatings, glasses, and other materials.

4.1 Processing Cell Mockup Studies

T. S. Mackey

The study of design concepts and process equipment is being continued in the processing-cell mockup. The mockup at present consists of the cell walls, two cubicles, two tank pits, manipulators, the intercell conveyor, the transfer area, and the cell-top mockup. The cell top was added to provide a means of studying remote maintenance problems in the tank pits and the operation of the equipment transfer case mockup. A hot disconnect well was made and installed to test jumper-line concepts. Service line connections to the equipment rack were also installed. Preliminary

testing revealed that minor alterations were necessary to simplify handling. New heavy-duty extended-reach manipulators were procured from Central Research Laboratory for testing the handling of heavy objects as required for maintaining the TRU equipment.

An equipment rack was built and fitted to three sets of tracks on the cubicle floor. Three sets of lifting arms, designed to aid in handling the racks, were installed on the cubicle ceiling. Counterweights were added to the lifting arms to make operation with the manipulator possible. Little difficulty was experienced in the preliminary testing of the rack-handling and positioning system. The equipment transfer case was completed, and initial adjustments were made to the door and hoisting mechanism. The cubicle top port was delivered and installed. A test device was used to demonstrate that the door latch seal, as designed, was capable of holding 20 lb/sq in. of air pressure without leakage.

Test work on the cell lighting system included the selection of the best location for the lights, measurement of the light intensity at various points, the selection of proper dimensions to permit installation and removal of the electric conduit, the establishment of the need for light reflectors, and the determination of the effect of heat from the lights on the manipulator booting material. The final design will include four mercury vapor lamps operating on separate ballasts, and two incandescent lights for color correction and emergency use. Each lamp bulb with its own protective cage will be supported by a hook mounted on the cell wall. Bulbs will be replaced by unplugging the power cord and then replacing the cord, porcelain lamp base, and lamp as a unit, eliminating the handling problems encountered in a multiple-bulb light fixture. A manipulator-booting-seal extractor was tested and performed satisfactorily. However, it was found desirable to apply talcum powder to the seal surface to decrease the friction as the seal is forced into place on installation of the first boot seal and on each succeeding one.

A method for removing the alpha window is being devised; it consists in (1) the removing of the segmented window frame and seal, (2) placing the window in a canvas bag, (3) shattering the window to reduce it to a

size that can be raised into the equipment transfer case, and (4) removing the bag through the case. Samples of annealed glass and tempered glass were tested for ease of handling. The tempered glass breaks into many small particles, which can be handled easily, and was selected for this reason.

4.2 Equipment Development

T. S. Mackey

Development of process equipment concepts were mostly completed, and many prototype units are being fabricated or tested. A mockup of the ion exchange column was operated; the ion exchange resin was held in place with a piston operated by hydraulic pressure. Flow rates were determined for optimum conditions for loading and unloading the exchange resin. Process liquid flow metering and control devices were successfully tested. Tests of a diaphragm sampler pump design demonstrated adequate performance and adequate life for Hastelloy-C or Zircaloy-2 diaphragms. Two sampler pumps were made and tested for the Building 4507 installation. Testing of a large number of disconnect samples showed that the machined insert design for the male core and the flared tube end were superior as an overall solution for the disconnect problem. With tantalum disconnects, it was necessary to burnish the seal surfaces with hardened steel rollers to minimize galling and effect a leak-tight joint.

An epoxy resin bond between fittings in a Fiberglas vent pipe was tested. The arrangement consisted of joints of pipe furnished by two manufactures, and the pipes were joined with epoxy glue. The assembly failed at 1100 psi. The pipe will be used at much lower pressures.

4.3 Solvent Extraction Contactor Development

F. L. Daley

The testing of flowsheets has continued in 3/4-in.-ID glass pulse columns packed with 48 in. of tantalum sieve plates (1/32-in. holes, 5% free area, spaced 1/4 in. apart).

As part of the Tramex flowsheet studies, scrubbing of fission products (europium tracer) from 30% Alamine 336 in DEB by a 9 M LiCl--1 N AlCl₃, was tested. At a total throughput of 12 ml/min, at 50°C, the best pulse conditions (frequency, 40 cpm; amplitude, 0.2 in.) gives column operation near the emulsion flooding point and results in an average stage height of 17 in. Operation at 70°C, using the same pulse conditions, did not significantly increase total throughput but resulted in a slightly lower height of 14 in. Overall performance was not improved by the addition of FX-170, a fluorochemical surfactant, to the aqueous phase. Total throughput increased threefold, but the stage height was increased by the same factor. It was necessary to raise the pulse frequency to 80 cpm and reduce the total flow to 12 ml/min to get a stage height of 24 in.

Tests were made at a constant organic flow rate and the aqueous flow controlled to give phase ratios (A/O) of 1/3, 1/2, and 1 to find the effect of phase ratio on stage height. No significant effect was noted. The plate spacing was increased from 1/4 to 1/2 in. No significant improvement in throughput was realized but the stage height was increased by a factor of 1.5

The extraction of nitrate from 5 M HCl--1 M HNO₃ by 30% Alamine 336 in diethylbenzene was studied. Batch phase-break tests (A/O of 1/1, aqueous phase continuous, at 25°C) gave a break time of 60 sec compared with break times of 150 sec at 25°C and 75 sec at 50°C for the Tramex process. Operation of the process in the 3/4-in.-ID glass pulse columns at 25°C resulted in the same solution throughput found for the Tramex flowsheet at 50°C (12 ml/min). Extraction of nitrate into 30% Alamine 336 in DEB (free amine form) resulted in a raffinate containing 0.0005 M HNO₃, which indicated a 12-in. stage height.

4.4 Evaluation of Protective Coatings

G. A. West

Radiation-damage tests made on protective coatings to determine the upper tolerable limits of exposure in air and in deionized water (at 40 to 50°C) to Co⁶⁰ gamma rays at an intensity of about 1×10^6 r/hr were

completed. The coatings were considered to be potentially useful in the TRU facility, where radioactive elements must be contained or easily removed from structural surfaces.

Fifty-four protective coatings were irradiated; 17 were resistant at and above 10^9 r while submerged in deionized water (Fig. 20), and 40 were resistant in air at 10^9 r. At 4×10^9 r, four coatings (epoxies or epoxy-phenolic formulations) were still serviceable in deionized water, and 26 in air. In general, the coatings were less affected by radiation when exposed in air than when immersed in deionized water.

The polyamide cured epoxy coatings had the best radiation resistance while immersed in deionized water. Of the 17 coatings resistant to greater than 10^9 r in deionized water, ten were epoxies, three were epoxy-phenolic formulations, three were modified phenolics (probably of the epoxy-phenolic formulation), and one was an inorganic coating. Most of the failures at the higher radiation levels resulted from embrittlement and chalking of the top seal coat, loss of adhesion, and a marked decrease in impact resistance. The coatings reinforced with Fiberglas fabric retained resistance to impact much better than the unreinforced coatings. Experimental formulations by the Sika Chemical Company and the Carboline Company, in which a dispersion of Fiberglas pigment was included in the coating, did not appreciably improve their resistance to radiation damage. The most severe attack on the submerged coatings occurred at the air-water interface, where extreme chalking, erosion, and softening were evident on most of the coatings.

Studies of the relative ease of decontamination of these coating systems were continued. Decontamination factors (DF) were determined for the various coatings by a water flush and a 3 M HNO_3 scrub at room temperature to remove mixed fission products (predominately Ce-Pr¹⁴⁴, Zr-Nb⁹⁵, and Ru¹⁰⁶) with an initial activity of about 3 r/hr. The highest DF, 9.33×10^3 , was obtained on a vinyl coating--U. S. Stoneware, R0221 with silicone, and TP216 top coat. An epoxy, Amercoat No. 66 gloss, gave the second highest DF (6.3×10^3). The highest and average DF's for the various types of coatings were as follows:

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Fig. 20. Protective Coatings Resistant to more than 10^9 r of Gamma Radiation.

EPOXY: Highest, 6300 (Amercoat No. 66 gloss); average of 19 coatings, 872
MODIFIED PHENOLIC: Highest, 1730 (Carboline Co., No. 300-finish, white);
average of 11 coatings, 415

POLYESTER: Highest, 2700 (Prufcoat, epoxy modified polyester); average
of three coatings, 1850

VINYL: Highest, 9330 (U. S. Stoneware, RO-221 with silicone, TP216 top
coat); average of 16 coatings, 988

INORGANIC: One coating tested, 63 (Amercoat, Dimecote No. 3)

The decontamination factors for the epoxy and modified phenolic
coating tabulated above are higher than for any tests made and reported
earlier.

5. DEVELOPMENT OF A FABRICATION PROCESS FOR HFIR TARGET ELEMENTS

D. A. Douglas

Most of the serious problems described in the last quarterly report
were successfully resolved. Pellets that show excellent thermal conduc-
tivity were made, and satisfactory welds can be achieved. The collapse of
the tubing and the attachment of the hex can were successfully demonstrated.
As a result, no difficulties were encountered in the fabrication of six
prototype targets for an irradiation experiment. Four of these are under
test in the Engineering Test Reactor (ETR).

5.1 Laboratory Research and Development

5.1.1 Pellet Preparation -- (D. M. Hewette, II)

A procedure for the fabrication of target pellets was developed; it
utilizes large particles of PuO_2 produced by a recently developed drying,
firing, and grinding procedure. Since this type of PuO_2 is a coarse, high-
density powder rather than the fluffy, finely divided oxide envisioned in
the original design concept,⁷ a re-evaluation was made of the previously
developed pellet-pressing procedure. The pellet configuration remains the

⁷D. E. Ferguson, Transuranium Quart. Progr. Rept. Feb. 28, 1962,
ORNL-3290, p 17.

same as the reference design,⁷ with the core being pressed inside a type 1100 aluminum tube and covered top and bottom by a 0.050-in.-thick type 1100 aluminum powder end cap. Large particle-size high-density PuO_2 is required in order to obtain a pellet core having a continuous aluminum matrix, and thereby, a high thermal conductivity. The larger-particle-size oxide also should reduce the fraction of fission fragments lodging in the matrix material. For example, experience with spherical UO_2 showed that with a particle size of $9.4\ \mu$, 100% of the fission fragments lodge in the matrix, while, with a particle size of $105\ \mu$, only 7% lodge in the matrix.⁸ Selection of the specific particle size range of -140 +325 mesh (44 to $108\ \mu$) for the PuO_2 was based on homogeneity studies done in connection with the HFIR fuel element.⁹

The pellet-pressing procedure re-evaluation was carried out by using -140 +325 mesh U_3O_8 as a substitute for PuO_2 . The study included a determination of pour density, blending time, composition variation from pellet to pellet, and pressing pressure required for producing pellets having densities of $89 \pm 3\%$ of theoretical. The pour density for a blend of 14 vol % of oxide was 1.5 g/cc or 48% of theoretical. This indicated that a 1-in.-long aluminum tube would provide sufficient volume to contain the loose core powders of the irradiation prototype pellet. A miniature oblique blender with a 60-cc volume and of a size convenient for glove box operations, was constructed. One hour was required to adequately blend 14 vol % -140 +325 mesh U_3O_8 with -100 mesh aluminum.

Several 1-rod batches of stand-in pellets were prepared in a mockup of the glove box. Weighing was done with a torsion balance that weighed to the nearest 0.01 g. Blending was accomplished by using the previously described miniature oblique blender. The pellet press incorporated a 10-ton hydraulic cylinder and an electrically driven hydraulic pump which applied a continuous load. To produce pellets with cores of the desired

⁸A. Boltax, "Behavior of Fissionable Material Under Irradiation," p 351 in Nuclear Reactor Fuel Elements Metallurgy and Fabrication, ed. by A. R. Kaufmann, Interscience Publishers, New York, 1962.

⁹W. J. Werner, personal communication.

density, a pressure of only 18 tsi was required; compared with the 30 tsi required for pellets containing about the same concentration of 0.6- μ -diam oxide.

The composition of these pellets varied by ± 5 wt % U_3O_8 , as determined by chemical analysis of six samples randomly chosen from a batch of pellets.

5.1.2 Thermal Conductivity Measurements -- (D. M. Hewette, II)

The thermal conductivity of 16 vol % -140 +325 Lindsay Mix oxide dispersed in aluminum was studied as a function of density. Thermal conductivities were determined at 125°C for specimens having densities of 71, 89, and 98.6% of theoretical; a thermal comparator apparatus was used.¹⁰ The results are listed below.

<u>Percentage of Theoretical Density</u>	<u>Thermal Conductivity (w/m-°C)</u>
71	31.3
89	138.1
98.6	177.8

The thermal conductivity for the 89%-dense dispersion in aluminum is nearly 10 times the value previously determined¹¹ for a 15 vol % -325 mesh Gd_2O_3 dispersed in aluminum. This large increase is ascribed to aluminum being the continuous phase in the case of the large-particle-size oxide, whereas the oxide was the continuous phase in the case of the oxide that consisted of very small particles.

5.1.3 End Closures for Target Rods -- (C. H. Wodtke)

The procedures for producing high-quality welded end closures must have a very high degree of reliability and yield reproducible results. Difficulties have been encountered in oxide stringering, scattered porosity, incomplete fusion to the root of the weld, and blowout of weld

¹⁰T. G. Kollie and D. L. McElroy, "A Thermal Comparator Apparatus for Thermal Conductivity Measurements from 40 to 400°C," p 289 in Conference on Thermal Conductivity Methods held at Battelle Memorial Institute, Oct. 26-28, 1961, BMI, Columbus, 1961

¹¹D. E. Ferguson, Transuranium Quart. Progr. Rept. Aug. 31, 1962, ORNL-3375, p 25.

metal due to entrapped gas. The studies during this reporting period were concentrated on methods for minimizing or eliminating these conditions. It appears that a precisely programmed welding cycle will be required. Therefore, a major part of the effort to date has been expended in obtaining and improving the following welding equipment:

1. Lathe for accurately rotating target specimens. This apparatus includes a speed reducer, rotation timer, and torch positioner.
2. Semiautomatic welding head for precise arc-length control.
3. Program-controlled welding power supply: 400-amp dc with automatic high-frequency arc starter, slope control, and gas control.

A timer unit for precise control of the steps not regulated by the existing equipment is on order as is an accurate, high-speed-of-response recorder.

Work to date has been confined to a relatively small number of welds in several groups of joints having various configurations. The welding conditions used for making the welds in the various groups are summarized in Table 5.1. Metallographic sections were made on welds that appeared visually to be good. As a summary, sections of welds representing four promising groups are presented in Fig. 21a, b, c, and d. In each case, the section shown is that of the best weld representing the group.

The work to date has demonstrated that welds exhibiting good external appearance and reasonably sound metallographic sections can be produced using several joint configurations. Consistency studies and mechanical-property tests will be conducted on the most promising joint configurations in order to further analyze the welds. An investigation of brazing as a secondary seal is also under way.

5.2 Fabrication of HFIR Target Prototypes for an Irradiation Experiment

5.2.1 Status of the Experiment -- (S. A. Rabin)

Fabrication and inspection of the six prototype irradiation target rods have been completed. Four of the rods, including the one containing the high-density pellets, have been shipped to Idaho Falls for irradiation in the MTR. Details of the rods are given in the following sections.

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Table 5.1 Welding Conditions Used in Making Welds in Various Groups

Weld Group	Joint Configuration and Electrode Angle	Control of Weld Cycle and Torch Type	Current at Start/Taper to (amps)	Weld Time to Start of Tail Slope (sec)	Rotational Data		
					Revolutions to Start of Tail Slope	Tube rpm	Type of Equipment
A		Manual and Stationary Torch	~60/~50	~8.4	~1-1/6	~8.3	Lathe
B		Automatic and Stationary Torch	~97/~52	~8.4	~1-1/6	~8.3	Lathe
C		Automatic and Stationary Torch	~90/~50	~8.4	~1-1/6	~8.3	Vertical Chuck
D		Automatic and	~90/~50	~8.4	~1-1/6	~8.3	Lathe
D		Stationary Torch	~110/~60	~8.4	~1-1/6	~8.3	Lathe
E		Automatic and Stationary Torch	~110/~60	~8.4	~1-1/6	~8.3	Lathe
F		Automatic and	115/70	~8.4	~1-1/6	~8.3	Lathe
F		Stationary Torch	110/65	~8.4	~1-1/6	~8.3	Lathe
G		Automatic and Semiautomatic Torch	200/120	1.4 - 1.5	1.4 - 1.5	60 = 1 rps	Lathe
H		Automatic and Semiautomatic Torch	225/125	1.4 - 1.5	1.4 - 1.5	60 = 1 rps	Lathe

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Fig. 21. Cross Section of Four Target Rod Welds.

The irradiation experiment has the general objective of serving as a proof test for the design, materials, and fabrication process. While it is recognized that the operating conditions in the MTR will not be as severe as those in the HFIR, answers to the more controversial features of the target rod design are expected. Some specific questions to be answered include: (1) Adequacy of heat transfer across the pellets and across the pellet-to-cladding gap. (2) Effect of cyclic thermal strains across the fins. We hope to resolve whether the current design, utilizing intermittent fins, is satisfactory; if not, full-length fins might be required. (3) The transmutation of type X8001 aluminum to silicon might become significant at the HFIR target burnups. One would anticipate some loss in ductility and corrosion resistance, although data suggest that one can be optimistic that adequate behavior will persist at high exposures. (4) Pressure buildup from gaseous fission products. Because of the pellet design, it is not known whether the fission gases can escape and migrate to the plenum at each end of the rod. (5) Swelling from solid fission products. Significantly, it was learned during a visit to Lawrence Radiation Laboratory that they have successfully irradiated many actinide oxide-aluminum dispersions in the MTR at exposures up to 4×10^{22} NVT with no swelling or bursting. (6) In-pile compatibility of PuO_2 with aluminum. Data are lacking.

The plans are to remove specimens after 6, 12, and 18 months. The shorter irradiation time will give lower burnups than desired but is necessary if any information is to be obtained prior to fabrication of the first loading of target rods.

5.2.2 Pellet Pressing for the Irradiation Experiment -- (D. M. Hewette, II)

One hundred forty-eight pellets containing 14 vol % PuO_2 in an aluminum matrix were pressed for the irradiation experiment. Eighteen of these will be used for control and evaluation. The pellets were pressed in batches of 28 so that each of six target rods would contain the correct loading. It was necessary to alter the fabrication procedure slightly from that develop in the laboratory because the PuO_2 had a particle-size range of -70 +325 mesh, as listed in Table 5.2, rather than the specified size range of -140 +325 mesh. Using a high-density thoria having a

particle size distribution as given in Table 4.2 as a substitute, the time required for blending a 14 vol % ThO_2 -Al mixture was found to be 2 hr. The thoria concentration varied from +4 to -10 wt % for nine pellets selected from a 28-pellet batch.

Table 5.2 Plutonium Oxide Particle Size: Screen Analysis

Screen Size (mesh)		Size (μ)	wt %
-70	+140	210-105	44.7
-140	+170	105-88	14.7
-170	+200	88-73	9.0
-200	+325	73-44	24.5
-325		0-44	7.1

The decision to use the coarse oxide was based on two factors: first, grinding the large-particle-size fraction to bring it into particle-size specification would produce about 25 wt % of -325 mesh size. Since only enough PuO_2 to make six rods was immediately available, this would be undesirable. Second, since the thermal conductivity of large-particle oxides dispersed in aluminum has been demonstrated to be fairly high, a variation in oxide concentration of ± 10 wt % should not be of serious consequence from a hot spot standpoint.

Although the pressure required to produce cores having 89 ± 3 % theoretical density for pellets containing the coarse thoria remained at 18 tsi, a pressure of 20 tsi was required for pressing the PuO_2 -bearing pellets to the same density. This increase in pressure was thought to be due to the presence of a small fraction of low-density oxide.

The percent theoretical densities obtained for the last five batches are summarized in Table 5.3. Unlike the preceding batches, batch 6 was pressed at a pressure that should yield pellets having the highest possible density.

Table 5.3 Densities of Irradiation Prototype Target Pellets

Batch No.	Pressing Pressure (tsi)	Average Percentage of Theoretical Density for 25 Pellets	Spread in Percentage of Theoretical Density
2	20	90.89	87.8-94.73
3	20	90.1	86.8-92.6
4	20	89.92	87.88-93.32
5	20	90.23	86.96-92.84
6	41	96.67	93.36-101.14 ^a

^aThis anomaly is probably due to oxide concentration variation from one pellet to another.

Two reject pellets were examined metallographically to confirm that a continuous aluminum matrix was achieved and to check for variation in oxide concentration from pellet to pellet. Aluminum was found to be continuous in both pellets. The PuO_2 exists for the most part as large high-density particles along with a small fraction of porous low-density particles. A comparison of representative photomicrographs taken of the two pellets showed the following: (1) The pellet from batch 5 contained 18 vol % oxide, while the pellet from batch 6 contained 11 vol % as determined by areal analysis performed on 14 different photomicrographs of each pellet. (2) Although the pellet from batch 6 had a low calculated percentage of theoretical density, very little void volume associated with the aluminum was observed. The observations of variation in oxide concentration from pellet to pellet and the lack of porosity in a pellet from a high-density batch having a calculated density of 88% of theoretical show that it is erroneous to calculate densities on individual pellets. A better basis for calculating the percentage of theoretical density for the target rod would be to use the entire pellet column since only the composition of the entire column is known.

5.2.3 Assembly and Inspection -- (J. D. Sease)

The prototypes (Fig. 22) although differing from the actual HFIR target in length and amount of fissionable material loading, were made

PELLET DETAIL

SECTION "A A"

Fig. 22. HFIR Target Radiation Prototype.

according to the methods proposed for the HFIR target elements. The prototype is 24 1/2-in. long, with an active fuel length of about 14-in., while the reference HFIR target element is 35 in. long and contains a fissionable loading 20 in. long. The assembly and fabrication of the elements were accomplished as planned with the exception of the final end-closure weld. The weld design and procedure used to make the end-cap welds is described in Sec. 5.3.4. The integrity of the weld was determined by leak testing and radiography. The first closure welds for the prototype were the best of a group of 20 welds. In the first attempt on the closure welds, all welds were leaktight; however, radiographic inspection showed only two acceptable and one conditional (control specimen) welds were obtained from 12 welding attempts. The rejected welds had void areas at the root of the welds, apparently caused by a pressure buildup inside the tubes. To alleviate this pressure buildup with the tube during welding, the next three welds were made after chilling the tube following insertion of the end plug. This procedure resulted in excellent quality welds. Radiographs of these welds, along with the other end welds, may be seen in Fig. 23.

During fabrication, no difficulties with transferable contamination were encountered. After the welding and collapse, the inspection and hex-can attachment were performed in a ventilated hood. The hex can was attached to the fin tubing by a simple punch method that deforms the hex can into the fin, effecting a mechanical joint.

The preirradiation data collected on each prototype include photographs of the rods at all stages of assembly, radiographs of the weld areas (three positions), a radiograph of the entire rod, the gross weight of the rod, length of rod, diameter of tube (seven positions), bow measurements, and tube-to-hex-can spacing. Figure 24a and b shows the fabricated fuel assemblies before and after attachment of hex can.

5.3 Development of Equipment for Fabricating Plutonium Targets

J. D. Sease and A. L. Lotts

Essentially all of the process equipment for the plutonium target fabrication line has been received and undergone initial tests. At the

545

540

11

8

5

2

(a) First Closure End Welds

545

540

11

8

5

2

(b) Final Closure End Welds

Fig. 23- Radiographs of Target Welds.

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Fig. 24. Fabricated Fuel Assembly. (a) Before and (b) After Hex-Can Attachment.

current rate of progress, the fabrication line should be operative by early 1964. A summary of the present status of the equipment follows.

5.3.1 Glove Boxes

The bag-out port fire shields on all the boxes received were modified after it was found that the as-designed shields were not satisfactory from an operational standpoint. The boxes containing the welding rig and the hydrostatic collapse rig were used in the fabrication of the irradiation samples.

5.3.2 Powder Preparation Equipment

An automatic dispensing-weighing machine will be incorporated in the powder preparation equipment to simplify the laborious hand dispensing-weighing operation. The weighing machine will be one similar to that designed for the TRU facility or a commercial one. Tests on the commercial unit, which uses vibratory feeding for dispensing, showed no segregation of an oxide-aluminum powder mixture and was satisfactory in weight reproducibility. A decision on the type of machine is awaiting the outcome of tests.

5.3.3 Pellet Preparation Equipment

A continuous pressing stroke which is desirable for wrinkle-free pellets was achieved by substituting an electric-driven pump for the original air-piston hydraulic pump. Pellets of excellent quality have been produced with the pressing equipment.

5.3.4 Tube-Closure Equipment

A programmed welding power supply that allows continuous control of the entire weld cycle was received and integrated into the welding procedure. The welding procedure that has been developed with the programmed welder fuses a step-type end cap onto the 3/8-in.-diam aluminum tube by the tungsten-arc process. The step-type end-cap weld design and setup used in the procedure may be seen in Fig. 25 (orig. dwg.). Before welding, the end plug is mechanically bonded to the tube by deforming the tube in the swaging groove. The unique feature of the weld design is the use of a machined lip as weld filler material. The massive aluminum heat

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1 CROSS SECTION BEFORE WELDING

2 CROSS SECTION AFTER WELDING

Fig. 25. Weld Design and Setup for Welding Step-Type End Cap.

sink used to extract heat from the weld zone has proved very satisfactory. A typical welding cycle developed for welding these end plugs may be seen in Fig. 26.

5.3.5 Hydrostatic Collapse Equipment

The hydrostatic collapse equipment, used to collapse the finned tube onto the pellets, was set up and tested. Using 20,000 psig pressure, a tube-to-pellet radial gap from 0.0005 to 0.001 in. was obtained when the initial radial gap was about 0.004 in.

5.3.6 Helium Leak-Test Equipment

The helium leak-test fixture was set up and evaluated. The test time cycle of the equipment is about 5 min.

5.4 Development of Equipment for Fabricating Targets in the TRU Facility

M. K. Preston R. I. Deaderick
A. L. Lotts

The basic criteria established for the target element fabrication process have changed little from those outlined in the first quarterly progress report.¹² Progress on this work is shown in Table 5.4. Some equipment concepts have changed, however, and equipment has been added or deleted as indicated by fabrication process development. These changes will be discussed in the equipment status report which follows.

Table 5.4 Percentage of Completion for the Design and
Fabrication of Equipment

Cubicle No.	Conceptual Design	Detailed Design	Equipment Fabrication
3	80	64	40
2	59	32	25
1	28	6	0
Overall percentage	55	34	21
Project percentage		36.7	

¹²D. E. Ferguson, Transuranium Quart. Progr. Rept. Feb. 28, 1962, ORNL-3290, p 36.

Fig. 26. Typical Weld Cycle.

5.4.1 Cubicle 3

The fabrication flow diagram for cubicle 3 has not changed; however, equipment is being added to facilitate the powder preparation and pelletizing operations. The equipment locations were changed slightly to provide wall mounting of the die and batch scales.

Aluminum Powder Addition Station. -- A conceptual study of a device that will facilitate the addition of aluminum powder to the calcined actinide was started. This is a new item of equipment deemed necessary to eliminate dusting when the aluminum powder is added.

Actinide Calciner. -- In a conceptual study, a front-loading 2000°F muffle furnace was tentatively selected for calcination of the actinides. Because of the size (approximately 24 x 24 in.) and configuration of the furnace, its location and accessibility are problems. Therefore, a round, top-loading muffle furnace that could be located in the front of the cubicle is being considered.

Blender-Dispenser. -- Fabrication of the blender-dispenser is complete, and bench testing has started.

Blender-Dispenser Elevating Mechanism. -- To properly attach the blender container to the blender-dispenser and to position the discharge nozzle over the die scale, the blender-dispenser must move 4 in. vertically. Detailed design of an elevating mechanism to perform this function is nearly complete.

Pellet-Load Scale. -- Fabrication of the prototype pellet-load scale is complete, and bench testing is under way. The difficulty noted previously with oscillation of the system was eliminated by selection of compatible components for the servo system that controls the balance. Accuracy of the prototype unit has been established at ± 3 mg. Joint operation with the blender-dispenser is to be conducted during the next quarter to verify the complete concept and prototype design before the final detail design is started.

Batch Scale. -- Design of the batch scale is awaiting the outcome of the pellet-load scale design.

Die and Batch Scale Support. -- Conceptual design of the wall-mounted support for the two in-cell scales is ready for approval.

Cap Powder Station. -- Fabrication of the cap powder station is complete, and bench testing is under way.

Die Assembly Feeder. -- Fabrication of the die assembly feeder was completed. Bench tests indicate that the design of the die magazines which are used in conjunction with the feeder must be revised.

Die-Holder Station. -- Conceptual design of the die-holder station was completed. The die-holder assembly is designed to grip the die assembly (containing the empty pellet tube and bottom cap) in such a manner that it can be moved into proper position and placed on the die scale platform in alignment with the blender-dispenser nozzle to receive the blended powder. The assembly consists of support legs and a funnel and is moved to the scale by the transfer arm.

Pellet Press. -- Bench testing of the pellet press was resumed after the installation of electrical equipment to control bottom punch discharge and to make some of the operations semiautomatic. The performance of the press is satisfactory.

Transfer Arm. -- Fabrication of the transfer arm was completed, and electrical motors and controls are now being connected for bench testing of the assembly.

Pellet Transfer Container and Discharge Device. -- The pellet transfer container was fabricated and satisfactorily tested. To eliminate the possibility of dropping the pellets onto the cubicle floor, a conceptual design has been developed for a device which will allow the pellets to be discharged into the ultrasonic cleaner under controlled conditions.

Pellet Ultrasonic Cleaner and Pellet Dryer. -- Detailed design of the pellet ultrasonic cleaner and drying equipment was completed. A conceptual study, seeking a new method for drying the pellets after cleaning, was initiated because of the excessive size of the drying and transfer units. Possible solutions to this problem are to dry the pellets in the ultrasonic cleaner or in the discharge chute of the ultrasonic cleaner during

the transfer into cubicle 2. Due to the possibility of this change, the detailed designs were not approved. The prototype ultrasonic unit and vibratory transfer track were received from the vendors and bench testing is under way. The transfer track is being reworked to better contain the pellets and eliminate some weld protrusions which stop the pellets during transfer. Tests conducted indicate the operations and concept to be satisfactory.

Equipment Mounting Base. -- Detailed design for the equipment mounting base was completed. Bids on fabrication are being obtained. The mounting base consists of a 2-in. sched-40, type 304L stainless steel pipe frame with top and bottom mounting pads for securing equipment to the base and the base to the cubicle floor, respectively.

Cubicle Crane. -- A conceptual design was developed for bridge cranes that are to be used in transferring heavy equipment in each cubicle. Motive power for the cranes was to be supplied by the in-cell manipulators; however, it now appears that positive drive of the bridge and trolley would be advantageous for more-reliable equipment handling. Therefore, additional conceptual studies are being made to develop drive units for the cell crane.

5.4.2 Cubicle 2

The fabrication flow diagram for cubicle 2 has changed as a result of moving the hydrostatic collapse equipment to cubicle 1. This equipment change will enable the rod to be x-rayed before collapsing so that the pellets in a tube with an unacceptable closure weld could be removed and placed in another tube. A report of the status of equipment in cubicle 2 follows.

Pellet Inspection and Loading Equipment. -- Fabrication of the pellet inspection and loading equipment was completed. The equipment is now being bench tested. This equipment consists of six basic components: two pellet feeders, a pellet diameter gage, a pellet stack-length track, pellet loading equipment, and the auxiliary enclosure that contains and positions the above components. Some redesign of the equipment will be required to permit the remote removal of certain components.

End-Cap Welding Equipment. -- Conceptual design of the end-cap welding equipment that will perform the functions of tube evacuation, helium filling, cleaning of the weld area, end-cap positioning, and tungsten-inert gas welding can now begin since a more reliable welding procedure and end-cap design has been developed.

Helium-Leak-Test System. -- Design and fabrication of the helium-leak-test system prototype was completed. Detailed design of the control console is now under way. Removal of the two absolute filters required in the in-cell system will be possible using joints sealed with double "O" ring seals. Such organic seals would be replaced with each filter change.

Target Ultrasonic Cleaner and Enclosure. -- Conceptual design of the target ultrasonic cleaner and target transfer enclosure was completed; detailed design is in progress. The target transfer enclosure, which is located inside the ultrasonic cleaning tank, will have the target rod placed inside by the transfer arm for cleaning. The enclosure is removed by the transfer arm and set on the enclosure trunnion for transfer of the target rod to cubicle 1.

Target Transfer Arm. -- Design of the target transfer arm is being held up pending a firm concept for an end-cap welding machine.

Equipment for Transfer of Targets from Cubicle 2 to Cubicle 1. -- A new concept for transfer of target rods through the intercell pass-through port into cubicle 1 was developed. The concept utilizes the target enclosure container, which is also used in the ultrasonic cleaner. The enclosure, which contains guide rails and rollers, is rotated by a trunnion motor to a position 20° below horizontal to connect with the transfer tube and valve located inside the pass-through port. The target pass-through tube contains guide rails, rollers, and shut-off valves and will allow the target rod to roll by gravity into a receiving chamber in cubicle 1. Detailed design was started on all components of the target transfer.

5.4.3 Cubicle 1

The fabrication flow diagram for cubicle 1 has changed in that the hydrostatic collapse equipment was moved into cubicle 1. This change was discussed in the cubicle-2 status outline. An additional helium-leak-test chamber will also be placed in the cubicle; the penetrant inspection equipment is to be eliminated since experiments with end-cap welds showed that examination with penetrant chemicals will reveal little information that is not already available from radiography and helium-leak testing.

A report of the status of equipment in cubicle 1 follows.

Target-Rod Receiver. -- Conceptual design of the target-rod receiver was completed and detailed design has started. This container will stop and retain the target rod as it is received from cubicle 2 and will rotate the rod to the vertical position. It can then be removed by the cubicle 1 transfer arm for subsequent assembly and inspection steps.

Target Rod Surface Smear. -- Conceptual design of a surface smear fixture is 75% complete. This fixture will consist of a support plate in which foam rubber pads are retained. The target rod will be pulled through the pads by the transfer arm as the rod is removed from the target rod receiver. Smear pads will then be sent out of the cubicle for measurement of transferable contamination.

Target Rod X-Ray Unit. -- Selection of the x-ray unit to inspect the closure weld had been withheld until the welding procedure and end-plug design were established. Criteria for a suitable unit are now being established on the basis of the recent experience with end-cap welding.

Target-Rod and X-Ray Film Holder. -- The criteria and target rod end-cap design previously established were used as bases for the conceptual design of the target rod and film holder. The concept will probably be satisfactory for the new criteria that are to be established for the changed rod design.

Target Dimensional Inspection Equipment. -- Conceptual design study of the equipment for target dimensional inspection has been conducted, but a firm concept has not been established.

Hydrostatic Collapse Equipment. -- Detailed design of the hydrostatic collapse equipment was completed; however, the equipment has not been fabricated. Development work is being conducted on a similar unit built for the plutonium target fabrication line. Experience with that unit indicated that the chamber seal should be redesigned for satisfactory containment during operation. Tests of the plutonium target collapse chamber, piping, and booster-pump installation have shown that the design is sound.

Hex-Can Installation Fixture. -- Conceptual design of a fixture for attachment of the hex cans to the finned tubes was started. The reference design of the target-rod assembly has been changed so that the tube fins are now attached to the corners of the hex can instead of to the flats.

Development tests of possible methods for positioning and attaching the can to the rod have included welding, brazing, roll swaging, and punching. A conceptual design is being worked on for the punching method, which consists of indenting the hex can with a chisel point, thereby deforming the can into the tube fins to effect a mechanical joint.

6. TRANSURANIUM PROCESSING PLANT DESIGN

W. E. Unger

6.1 Hot Development Facility, Cells 3 and 4, Building 4507

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6.1.1 Cell 4

The installation of equipment and piping in the makeup area, operating area, and the cell is complete. The equipment in the roof area will be completed by October. The makeup area equipment is being checked out and calibrated by the operating personnel. The operating area and cell will be released to the operators in the middle of September.

Figure 27 is a photograph looking from the operating area into the cell. To allow access during construction, the mixer-settler rack-piping jumpers are not connected.

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Fig. 27. View through Cell Windows.

Figure 28 is a photograph, taken from the cell roof, of the two tanks in front of the mixer-settler rack. The piping-jumper concept is very clearly shown in this photograph. The accessibility of the disconnect clamps and jumpers will greatly ease the task of modifying the cell components.

6.1.2 Cell 3

The design of cell-3 components was started, as was the procurement of some items. The main items are the dissolver; a condensate catch tank; and a rack of equipment consisting of an overhead condenser, scrubber, iodine trap, filter, and pump. These will be designed for easy removal from the cell by rolling into position beneath the existing large equipment opening in the roof of the cell.

The remainder of the cell will be used for work-table space and a service-disconnect bank for the experimental equipment boxes that are to be placed in the cell. Boxes will be transferred into and out of the cell through the roof opening, using alpha bagout techniques. These boxes will contain laboratory equipment for testing process conditions and support experimentation for cell 4, as well as for testing new processes requiring alpha-gamma shielding.

6.1.3 Americium-Curium Unloading-Station and Storage System

Shipment of the americium-curium-rare-earth solution from the Savannah River TRU irradiations necessitated the installation of a temporary unloading station at Building 4507.

This installation is shown in Fig. 29. The glove box and shielded piping will permit the present tank, T-30, to be used for holdup of the feed solution for later processing in cell 4. The glove box and the piping from the carrier to the valve containment box will be removed after the transfer has been made.

The valve-containment box will provide access for addition of solutions to T-30 or any of the cells in Building 4507 at a future date if required.

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Fig. 28. View through Equipment Chute in Cell Roof.

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Fig. 29. Unloading Station.

6.2 Design of Chemical Processing Equipment

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E. J. Breeding	

6.2.1 Flowsheets

A set of 16 engineering flowsheets showing the TRU process equipment were completed and issued. The equipment flowsheets were revised to reflect changes incorporated into the engineering flowsheets. The equipment flowsheets, in simplified form, are shown in Fig. 30 and Fig. 31.

6.2.2 Detailed Design at ORGDP

The design of the chemical process equipment by the ORGDP (Oak Ridge Gaseous Diffusion Plant) engineering group is about 33% complete, with 11 men working on detailed design. Forty-seven approved drawings were issued. Final drawings were approved and issued during the quarter for the six equipment items discussed below.

Process Pumps. -- The process pump design for the TRU development facility¹³ in Building 4507 was revised to incorporate an improved air drive shut off valve and to modify the disconnect blocks for a specific application in the TRU samplers.

Sampler. -- A 12-unit sampler (Fig. 32) will be installed in each of the four chemical processing cubicles, occupying the bottom half of the back equipment racks. The sampler can be removed from the back equipment rack to permit individual replacement of either the equipment rack or the sampler station. Solution is recirculated through a sample bottle by a TRU process pump. A mechanical linkage is used to elevate the sampler bottle onto the sample needles. The needle block and bottle lift are located inside a ventilated housing, equipped with a water spray for washing down the sampler after each sampling operation. The 12 sampler pumps in a station are driven by a single air drive line with individual valves incorporated into each pump. A single sampler unit will be

¹³D. E. Ferguson, Transuranium Quart. Progr. Rept. Nov. 30, 1962, ORNL-3408, pp 74, 75.

Fig. 30. Flowsheet for Equipment Used in Processing Targets (Cell 7).

Fig. 31. Flowsheet for Equipment Used in Processing Targets (Cell 6).

Fig. 32. Sectional Elevation of Sampler.

"mocked up" to test the bottle lift mechanism and the flow characteristics through the needle block before construction of the four sampler stations.

Dissolver. -- The dissolver for the TRU facility is identical in design (Fig. 33) to the one to be installed in the Building 4507 development facility. The dissolver must withstand 2 to 6 M HCl at temperatures ranging from 50 to 110°C. Zircaloy-2 was chosen as the construction material in order to minimize hydrogen embrittlement and to allow partial dejacketing of the targets by caustic. The dissolver is designed for an aluminum dissolution rate of 1 g/min.¹⁴ A bid request has been issued to obtain one dissolver unit for installation in Building 4507.

Dissolver and Feed Solution Filter. -- Filtration of the dissolver and adjusted feed solutions is necessitated by the presence of silica and plutonium solids in the solutions. The filter consists of a Zircaloy-2 housing with Pyrex elements bonded to Zircaloy-2 tubes (Fig. 34). The filter will be mounted on the back equipment rack in cubicle 7 as part of the feed makeup system (Fig. 30). The six Pyrex filter elements provide a filter area of 47 in.², which, when clean, will pass 20 to 25 liters/hr of 10 M lithium chloride. The filter unit can be transported in the inter-cell conveyor and is installed on the equipment rack by a single mounting bolt.

Cubicle Disconnect Well and Cubicle-to-Pit Line Bundle. -- The design of the disconnect wells and associated cubicle-to-pit line bundle support structure for cells 4 through 7 was completed. The lines in the bundle will be detailed as part of the cell and cubicle piping. The present design includes the tracks required for remote replacement of the well and line bundle. A prototype of the disconnect well and line bundle is presently being built for installation in the TRU mockup to test the remote removal and replacement concept, previously described.¹⁵

¹⁴D. E. Ferguson, Transuranium Quart. Progr. Rept. Nov. 30, 1962, ORNL-3408, pp 74, 75.

¹⁵D. E. Ferguson, Transuranium Quart. Progr. Rept. Feb. 28, 1962, ORNL-3290, p 53.

Fig. 33. All-Zircaloy-2 Dissolver.

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Fig. 34. Feed Solution Filter, F-70.

First-Cycle Solvent Extraction System: The design of the left equipment rack for cubicle 7, which contains the first-cycle solvent extraction system was completed, and construction of the equipment was started in the ORNL shops. The equipment on the rack includes three pulse columns, with a 5-ft active section in each. Also, mounted on the rack is the associated feed system, pulsers, hold tank for process streams, and control jacklegs. All vulnerable components such as pumps, valves, and the columns are mounted on the front of the rack for simplified remote replacement with the equipment rack in place in the cubicle. The solvent extraction system is designed for a feed rate of about one l/hr at flowsheet condition. About a day of operation will be required to process each target.

6.2.3 Disconnect Design

The TRU disconnect clamp (Fig. 35) has been modified to provide a positive opening and closing motion to the top clamp and to simplify the removal of the top clamp and bolt assembly. The latter feature is required to permit removal of some of the short cubicle jumper lines. The stud and nut of the original clamp¹⁶ were replaced by a bolt, and was made "captive" to the bolt by a spring-retainer ring. The top clamp arm is forced closed by a cam arrangement on the bottom casting; this forces the top clamp closed as the bolt is tightened. The cam is opposed by a spring, recessed into the top clamp, which opens the clamp as the clamp is raised by the bolt to clear the cam. Drawings of the disconnect ferrules are being revised to reflect minor changes in tolerances and dimensioning procedures.

6.2.4 Waste and Off-Gas Headers

A change in design and construction material of the waste and off-gas headers in the cell bank, and upgrading of these headers from Hastelloy C to Zircaloy-2, was made as a result of recent corrosion data which gave corrosion rates as high as 100 mils/month. The change in design is consistent with the latest concept of intercell piping and permits remote replacement of both the waste and off-gas headers, a feature not included in the original design. The headers run the length of the cell bank with 3/4-in.

¹⁶D. E. Ferguson, Transuranium Quart. Progr. Rept. Nov. 30, 1962, ORNL-3408, pp 79, 80.

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Fig. 35. Modified Disconnect Clamp.

tubing connections saddle welded into the 1-3/4-in.-OD by 0.120-in.-thick wall header for process connections in each cell. The headers terminate in cell 7 (Fig. 36) where the off-gas header is connected to the inlet of the caustic scrubber (L-131). A low place in the off-gas header in cell 7 drains into the waste header. A diversion system on the waste header in cell 7 permits routing solutions either to the rework tank (T-77) or the waste collection tank (F-115) in cell 8. Air pressure applied to the jackleg maintains a liquid level in the rework drain line sufficient to prevent flow into T-77 and forces solutions to F-115 in cell 8. When pressure to the jackleg is reduced, the low point in the waste header drains to the rework tank. The bleed orifice in the pressurization line ensures that air flow is always into the cell through the pressurization line.

The waste header penetrates the cell partition walls as part of the intercell piping plugs, with disconnects on either side of the partition and a jumper section spanning each cell. This permits replacement of individual sections of the waste header and simplifies the overall concept of the intercell piping. The off-gas header is above the cell piping and passes through a plate at the cell partitions which provides a seal between cells. A single disconnect in each cell permits remote replacement of the header, but individual sections cannot be replaced without disturbing adjacent sections. Enlarged versions of the TRU disconnect concept were designed and tested for making the required connections in the tubing used for the headers. The waste header uses a block design with a yoke-type clamp; a single 1-in. bolt provides the sealing force (Fig. 37). The off-gas header connection uses the same disconnect surface design, but the sealing force is provided by a union-type coupling.

6.3 Design of the TRU Processing Plant

D. F. Bottenfield	G. B. Berry
B. B. Klima	F. L. Hannon

6.3.1 Building Design

The lump-sum contract for construction of the TRU Processing Plant was let to Blount Brothers Construction Company of Montgomery, Alabama,

Fig. 36. Waste and Off-Gas Headers - Cell Pit 7.

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Fig. 37. Waste-Header Disconnect Assembly.

on June 12, 1963, in the amount of about \$2,560,000. Notice to proceed with construction was given, effective July 1. Since that time the area was cleared; rough grading completed; excavation for the cell bank and pipe tunnel completed; and installation of the sanitary and storm sewer system is well advanced.

Procurement of materials by ORNL to furnish the contractor is proceeding nearly on schedule. Cost-plus-fixed-fee contracts were established with KPT Manufacturing Company of Roseland, New Jersey, for fabrication of the cell viewing-window sleeves and the alpha-seal window assemblies for the cell-viewing window. Corning Glass Works (Corning, New York) was the successful bidder on a lump-sum contract to supply the bulk shielding window assemblies. A cost-plus-fixed-fee contract was established with Nooter Corporation of St. Louis to fabricate an engineering model (full scale) of the Hastelloy C cell-cubicle floor pans, and S. Blickman and Sons of Weehawken, New Jersey, was awarded the lump-sum contract for fabrication of the intercell conveyor housing.

6.3.2 Mechanical Equipment Design

Intercell Conveyor. -- A test section of the conveyor housing was made by S. Blickman to investigate shrinkage when sections will be welded together in field. Three welds indicated a uniform shrinkage of $3/32'' - 1/8''$ per joint. Most of the certifications, procedures, and welder qualifications have been submitted to ORNL for approval. Layout and forming of the material has started.

Drawings and specifications have been transmitted to UCND Purchasing for distribution.

Equipment Transfer Case. -- Fabrication of this item was completed, and the case was transferred to the Y-12 Mockup where it is undergoing testing to evaluate leak tightness, mechanical operation and handling capabilities.

Cell Cubicle. -- The cubicle cooling-system design proposed by Plant and Equipment Division was reviewed and approved by Chemical Technology Division. Detailing of the equipment is in progress. The cubicle lighting was reviewed, and it was agreed that individual ballasts to serve

each lamp would be desirable. Appropriate changes will be made in the Catalytic drawings.

Carrier Charging System. -- Concepts of this system were reviewed and approved. The concepts were based on the use of disposable canisters; designs of these canisters have been issued to prospective fabricators. A second phase of this program, started during this period, is a study involving the handling and disposal of waste materials on discharge from the cell bank, assuming that these materials are to be transferred either to the burial ground or to the decontamination room.

6.4 Critical Path Scheduling

C. H. LaMaster B. N. Robards

A thorough re-evaluation of the ORNL design schedule was made in July, 1963. As a result, critical-path-schedule arrow diagrams for design were redrawn, and new schedules and projected progress curves were generated. An analysis of these schedules revealed a significant increase in the overall manpower estimates, primarily in conceptual and preliminary design of Target Fabrication Equipment (Table 6.1). The new revisions are based on more-refined estimates and plans that have been developed through preliminary design completed to date. The redrawn arrow diagrams were photographed and reduced to facilitate handling.

Changes were made in the monthly design progress report to permit not only periodic progress reporting of total design, but also individual progress reports on the three major phases of design effort: Chemical Processing Equipment, Mechanical Equipment, and Target Fabrication Equipment. Progress will continue to be reported graphically once a month on a preset curve based on probable completion of remaining work. The schedule will be updated and recomputed at any time it is determined that variances significantly affect the accuracy of the report curve. A copy of the newly generated progress curve for total design is shown in Fig. 38.

A Summary Critical Path Schedule (Fig. 39) was prepared for the Atomic Energy Commission June 24, 1963, and updated and issued the second time on September 1. The schedule, planned for presentation quarterly,

Fig. 38. Probable Progress of the ORNL Transuranium Design Work.

Fig. 39. Summary Schedule for the TRU Processing Plant.

is aimed at presenting only the salient details affecting the schedule in the interest of overall simplicity.

Table 6.1 Manpower Requirements:
ORNL Design as of August 1, 1963

	Man-Days			
	Previous Estimate	New Estimate	Expended	% Complete
Chemical processing equipment	4,355.00	4,191.00	1,192.50	28.45
Mechanical equipment	1,792.00	2,835.30	1,523.00	53.72
Target fabrication equipment	1,307.00	4,829.50	1,730.00	35.82
Total	7,454.00	11,855.80	4,445.50	37.02

Study → *For TRU Plant*

7. CORROSION STUDIES

J. L. English J. C. Griess

7.1 Corrosion of Zircaloy-2 by Mixed Acids

A survey was undertaken to examine the corrosion behavior and the sensitivity to hydrogen pickup of welded Zircaloy-2 in oxygenated hydrochloric-nitric acid solutions at temperatures of 43 and 110°C. The latter was the approximate atmospheric boiling temperature of the test solution, which consisted of 3 and 6 M HCl that were 0, 0.1, and 0.5 M in HNO₃. Tests were continued for a total of 1000 hr, with solution replacements at 100-hr intervals. Observed corrosion rates are reported in Table 7.1, along with the hydrogen content of the specimens after the 1000-hr exposure.

With the exception of the 3 M HCl--0.5 M HNO₃ environment at boiling temperature, corrosion rates were quite acceptable -- 0.5 mils/month and less, in the 3 M HCl tests -- under all conditions. A rather high rate of 3.3 mils/month was obtained on a specimen exposed in the solution phase of the 3 M HCl--0.5 M HNO₃ environment. There were no indications of hydrogen pickup in any of the specimens exposed in solution. Hydrogen contents were not determined for those specimens exposed to the vapors.

Table 7.1 Corrosion of Welded Zircaloy-2^a by Oxygenated Hydrochloric Acid Solutions Containing Nitric Acid Additions

Duration of Test: 1000 hr

Environment	Temp (°C)	Specimen Location	Corrosion Rate (mils/month)	Hydrogen Content ^b (ppm)
3 <u>M</u> HCl	43	Solution Vapor	< 0.1 < 0.1	20 -
3 <u>M</u> HCl-0.1 <u>M</u> HNO ₃	43	Solution Vapor	< 0.1 < 0.1	47 -
3 <u>M</u> HCl-0.5 <u>M</u> HNO ₃	43	Solution Vapor	0.5 0.2	47 54
3 <u>M</u> HCl	110	Solution Vapor	< 0.1 < 0.1	47 -
3 <u>M</u> HCl-0.1 <u>M</u> HNO ₃	110	Solution Vapor	0.1 0.3	54 -
3 <u>M</u> HCl-0.5 <u>M</u> HNO ₃	110	Solution Vapor	3.3 0.4	44 -
6 <u>M</u> HCl	43	Solution Vapor	< 0.1 < 0.1	40 -
6 <u>M</u> HCl-0.1 <u>M</u> HNO ₃	43	Solution Vapor	1.2 0.1	48 -
6 <u>M</u> HCl-0.5 <u>M</u> HNO ₃	43	Solution Vapor	0.2 0.1	43 -
6 <u>M</u> HCl	110	Solution Vapor	0.2 < 0.1	89 -
6 <u>M</u> HCl-0.1 <u>M</u> HNO ₃	110	Solution Vapor	1.6 0.4	440 -
6 <u>M</u> HCl-0.5 <u>M</u> HNO ₃	110	Solution Vapor	0.2 0.4	50 -

^aInitial hydrogen content varied between 38 and 53 ppm.

^bHydrogen content in specimen after 1000-hr-test.

In the 6 M HCl tests at 43°C, a maximum corrosion rate of 1.2 mils/month occurred in the solution containing 0.1 M HNO₃. There was no hydrogen pickup in any of the tests. At boiling, a maximum rate of 1.6 mils/month was observed, again in the solution containing 0.1 M HNO₃. The solution-exposed specimen contained 440 ppm of hydrogen; 38 to 53 ppm were present initially. A slightly high content of 89 ppm was found also in the specimen exposed to the boiling 6 M HCl solution.

Additional data were obtained on the sensitivity of Zircaloy-2 to hydrogen pickup in boiling acid solutions. In the supplementary tests, specimens in an unwelded condition were prepared from vacuum-annealed 10-mil-thick strip that contained 260 ppm of hydrogen. The previously described tests were carried out with specimens prepared from an as-received 125-mil-thick heat of Zircaloy-2.

Tests were conducted for 1000 hr in boiling and oxygenated 6 M HCl and in 6 M HCl--0.1 M HNO₃ solutions with the 10-mil-thick specimens. After exposure in 6 M HCl, a solution-exposed specimen contained 5300 ppm of hydrogen, compared with 89 ppm found in a 125-mil-thick specimen of the alloy exposed to a similar test. The observed corrosion rate for the 10-mil-thick specimen was 0.9 mils/month; the companion 125-mil-thick Zircaloy-2 specimen corroded at a rate of 0.2 mils/month during the same period.

The hydrogen content of a solution-exposed 10-mil-thick specimen after 1000 hr in boiling 6 M HCl--0.1 M HNO₃ was 2600 ppm, and the corrosion rate was 0.5 mils/month. In a similar test, a 125-mil-thick specimen corroded at a rate of 1.6 mils/month, and the final hydrogen content was 440 ppm.

The difference in specimen thickness of the two Zircaloy-2 heats undoubtedly contributed to the significant difference in observed final hydrogen contents, and metallographic study is being undertaken in an effort to further resolve the behavior.

7.2 Corrosion of Zircaloy-4 by Acid Solutions

Specimens of Zircaloy-4 rods, 125 mils in diameter, were exposed in several boiling and oxygenated acid solutions to determine if the

corrosion behavior and resistance to hydrogen pickup were superior to that of Zircaloy-2. The Zircaloy-4 heat contained less than 20 ppm of nickel, compared with a nominal value of 550 ppm generally present in Zircaloy-2. The hydrogen content of the heat was 19 ppm.

After 1000 hr in boiling 6 M HCl, which was replaced with fresh solution at 100-hr intervals, a solution-exposed specimen of Zircaloy-4 corroded at a rate nearly ten times faster than Zircaloy-2 in a similar test. The final respective rates were 1.9 and 0.2 mils/month. The final hydrogen content in the Zircaloy-4 specimen was 1000 ppm, whereas a pickup of 89 ppm from 38 to 53 ppm initially present occurred in a companion 125-mil-thick Zircaloy-2 specimen.

The corrosion resistance of Zircaloy-4 in boiling 6 M HCl--0.1 M HNO₃ was slightly better than that of Zircaloy-2 in a similar test. The 1000-hr rates were 1.0 and 1.6 mils/month, respectively. Some improvement was observed also in the resistance of Zircaloy-4 to hydrogen pickup. The 125-mil-diam rods specimen showed a hydrogen content of 130 ppm after test, while a specimen of Zircaloy-2 of similar thickness in a similar test exhibited a final hydrogen content of 440 ppm.

7.3 Corrosion of Hastelloy C by Mixed Acids

The effect of small additions of nitric acid on the corrosion of welded Hastelloy C by oxygenated 3 and 6 M HCl solutions was examined. Earlier work had demonstrated that an acid mixture, 1 M in HNO₃ and 3 M in HCl resulted in a marked improvement in corrosion resistance, compared with the behavior in the absence of nitric acid. For example, the rate was reduced from 7.3 to 0.7 mils/month when the nitric acid was added. The present tests were concerned with the effect of much smaller additions of nitric acid on the corrosion resistance of the alloy in hydrochloric acid solutions.

Table 7.2 summarizes corrosion data for both solution and vapor exposure. All test solutions were replaced at 100-hr intervals. For the most part, the rates represent average values for duplicate specimens. In cases where excessive corrosion was encountered, the tests were terminated after a relatively short exposure period.

Table 7.2 Effect of Nitric Acid on the Corrosion of Welded
Hastelloy C by Oxygenated Hydrochloric
Acid Solutions at 43°C

HCl Conc'n (M)	HNO ₃ Conc'n (M)	Exposure Time (hr)	Specimen Location	Corrosion Rate (mils/month)
3.0	0	1000	Solution Vapor	7.3 0.7
	0.01	500	Solution Vapor	11.9 0.8
	0.05	600	Solution Vapor	4.5 0.3
	0.10	400	Solution Vapor	7.0 0.2
	1.0	336	Solution Vapor	0.7 0.2
6.0	0	1000	Solution Vapor	5.5 5.3
	0.01	300	Solution Vapor	15.4 24.1
	0.05	100	Solution Vapor	58.5 67.5
	0.10	100	Solution Vapor	97.6 38.3

When 3 M HCl was made 0.01, 0.05, or 0.10 M on HNO_3 , there was no improvement in corrosion resistance, compared with results obtained in the absence of nitric acid. With nitric acid present, corrosion rates for solution-exposed specimens ranged from 4.5 to 11.9 mils/month; in the absence of nitric acid the rate was 7.3 mils/month. When the mixture was 1 M in nitric acid, however, a tenfold improvement in resistance was obtained; the 336-hr rate was 0.7 mils/month. Of additional significance was the fact that no preferential attack took place in heat-affected zones adjacent to welds on specimens exposed to the 3 M HCl--1 M HNO_3 environment. In all other tests, this type of attack was severe.

Vapor-phase corrosion in the 3 M HCl tests was little influenced by the absence or the presence of nitric acid in any concentration. Rates varied from 0.2 to 0.7 mils/month. With the exception of the vapor specimen in the 3 M HCl--1 M HNO_3 test, the other specimens exhibited a mild susceptibility to heat-affected-zone attack adjacent to welds.

The corrosion rates in the 6 M HCl solution with nitric acid present were considerably greater, both in solution and in vapor, than those in the 3 M HCl tests. As the nitric acid concentration was increased from 0.01 to 0.1 M, the rate for solution-exposed specimens increased from 15.4 to 97.6 mils/month. In the absence of nitric acid, the observed rate was 5.5 mils/month. Vapor-phase rates ranged between 24.1 and 67.5 mils/month with nitric acid present; with no nitric acid in the solution, the rate was 5.3 mils/month. Unusually severe heat-affected-zone attack was experienced by all specimens exposed to nitric acid-containing solutions. In a number of cases, the attack was sufficient to cause complete separation of the 125-mil-thick specimens at the weld-base metal interface.

7.4 Behavior of Tantalum-Plated Specimens in 6 M HCl

Two tantalum-plated specimens have received a total exposure of 1300 hr in boiling and oxygenated 6 M HCl solution. In one case, the tantalum was plated directly onto stainless steel base metal. The second specimen of Hastelloy C base metal was plated with a 0.3-mil-thick flash coat of copper before the tantalum was applied.

During the first 800 hr of exposure, the behavior of both plated specimens was excellent. However, in the period between 800 and 900 hr, a blister developed on the stainless-steel base-metal specimen. Subsequent examination showed the blister to be about 125 mils in diameter. During an additional 200 hr of test, the blister increased to nearly 200 mils in diameter. After a total of 1300 hr, no further increase in size was noted.

The appearance of the blister after 1100 hr is shown in Fig. 40. The location of the defect may be described in the following manner. The appearance of the specimen suggests that during the original plating operation, about three-fourths of the coupon was plated, after which the electrode was removed from one end, the specimen inverted with electrode re-attached to the opposite end, and the plating completed. The location of the blister was along the interface where one plate overlapped the other.

No penetration of the blister to the base plate took place, as substantiated by the fact that the test solution contained negligible amounts of iron and nickel, two of the elements present in stainless steel. The companion plated specimen remained in excellent condition during the 1300-hr test.

7.5 Behavior of Hastelloy C in Organic Processing Solutions

Tests of 1000 hr duration were completed with welded specimens of Hastelloy C exposed in the solution and vapor phases of two TRU organic processing solutions at 43°C. The solutions were 1 M mono-2-ethylhexyl-phenylphosphonic acid in diethylbenzene and 30% Alamine 336 hydrochloride in diethylbenzene. The solutions were changed every 100 hr.

The corrosion behavior of the specimens was excellent. In all cases, observed penetration rates were less than 0.1 mils/month, and there was no evidence of preferential attack in heat-affected zones adjacent to welds.

Fig. 40. Blister on Tantalum-Plated Stainless Steel Specimen.
Magnification about 4X.

7.6 Behavior of Homalite CR-39 in TRU-Related Environments

Solution and vapor specimens of Homalite CR-39, an allyl diglycol carbonate type of plastic, were exposed at 55°C in (1) oxygenated 6 M HCl, (2) oxygenated 8 M HCl, and (3) oxygenated 11 M LiCl--0.7 M HCl. Test solutions were changed at 100-hr intervals.

Table 7.3 summarizes the observed weight and dimensional changes for specimens in the three environments. The plastic was incompatible with the oxygenated 6 and 8 M HCl solutions. Severe weight and dimensional losses were encountered and the specimens, particularly those exposed to solution, were very gummy upon removal from test. After air drying, the specimen surfaces developed a highly crazed appearance.

Satisfactory behavior was exhibited by specimens in the LiCl-HCl environment. Minor weight and dimensional changes were obtained.

8. DEVELOPMENT OF ANALYTICAL METHODS

L. T. Corbin

J. C. White

8.1 Direct, Non-destructive Method for the Determination of Californium²⁵²

F. L. Moore

J. S. Eldridge

Work on this method was completed, and a final report was prepared. The abstract is given below.

A new, direct, nondestructive method for the determination of Cf²⁵² is described. The method is based on gamma scintillation spectrometry involving the measurement of prompt gamma rays coincident with the spontaneous fission of Cf²⁵². Cf²⁵² has an alpha half-life of 2.55 yr and a spontaneous fission half-life of 66 yr. The gamma ray spectrum in coincidence with the spontaneous fission extends to about 5 Mev. Each fission event yields an average of 10 to 12 gamma rays. The method may be used either for the rapid qualitative or quantitative determination of Cf²⁵² in the presence of associated fission products and actinide elements. As little as 10⁻² nanograms of Cf²⁵² can be quantitatively measured. Several useful analytical and process applications are discussed.

Table 7.3 Behavior of Homalite CR-39 in TRU-Related Environments

Environment	Location of Specimen	Physical Property Measured	Change (%)
300 hr at 55°C in oxygenated 6 <u>M</u> HCl	Solution	Weight	-31.86
		Thickness	-26.25
		Width	-4.69
		Length	-1.96
	Vapor	Weight	-11.16
		Thickness	-9.58
		Width	-0.57
		Length	-0.40
100 hr at 55°C in oxygenated 8 <u>M</u> HCl	Solution	Weight	-29.60
		Thickness	-24.78
		Width	-4.06
		Length	-1.60
	Vapor	Weight	-15.23
		Thickness	-12.50
		Width	-1.49
		Length	-0.71
300 hr at 55°C in oxygenated 11 <u>M</u> LiCl-0.02 <u>M</u> HCl	Solution	Weight	0
		Thickness	+0.85
		Width	-0.08
		Length	-0.18
	Vapor	Weight	+0.23
		Thickness	+0.17
		Width	-0.25
		Length	-0.11

8.2 Determination of Free Acid in Tramex Process Solutions

D. A. Costanzo

A polarographic study was undertaken to determine its applicability to the determination of free acid in Tramex process solutions which contain aluminum. The potentiometric titration method generally employed for the determination of free acid requires the use of a complexing agent to prevent the hydrolysis of the hydrolyzable cation during the titration of the acid with base. In the polarographic method the use of complexing agent is not required.

In this study the dropping mercury electrode was used. The effect of lithium chloride concentration (0.56-13.2 M) upon the half-wave potential ($E_{1/2}$) and upon the ratio of the diffusion current to concentration (I_d/C) for hydrogen ion was determined. The half-wave potential shifted linearly to a less negative potential, and the I_d/C decreased nonlinearly in magnitude with an increase in lithium chloride concentration. For a solution containing 2 millimoles of HCl, the shift in $E_{1/2}$ vs the S.C.E. is from -1.67 v in 0.56 M LiCl to -0.96 v in 13.2 M LiCl, and the decrease in I_d/C is from 8.7 to 1.5 μ a/millimoles, respectively. At a given concentration of lithium chloride I_d/C was constant over the concentration range studied, 1 to 10 millimoles H^+ . Aluminum does not interfere. For a given concentration of hydrogen ion the diffusion current remained constant with increase in aluminum chloride concentration.

Aluminum ion also exhibited an analytically useful reduction wave in concentrated solutions of lithium chloride. The half-wave potential for aluminum is -1.55 v in 11.2 M LiCl, compared with -1.85 v in 0.56 M LiCl. I_d/C for aluminum in 11.2 M LiCl is approximately 5 μ a/millimoles. The shape of the irreversible wave was observed to be dependent upon the acidity. In acid solution of 11.2 M LiCl, I_d/C was constant over the concentration range studied, 1 to 10 millimoles $AlCl_3$.

The polarographic studies will be continued in order to determine the possible interferences by other hydrolyzable cations for the determination of free acid in simulated Tramex process solutions. Also the

polarographic behavior of the rare earths and other electroactive ions at the dropping mercury electrode will be studied in concentrated solutions of lithium chloride.

8.3 Evaluation of Arsenazo III as a Reagent for Use in the Transuranium Program

D. A. Costanzo

H. Kubota

The spectrophotometric determination of the rare earths, thorium, and zirconium with Arsenazo III[1,8-dihydroxy-3,6-disulfo-3,7-bis(2'arsono-phenyl-azo)naphthalene] was evaluated. Conditions for the determination of rare earths are pH 2 to 3 and for thorium and zirconium 1 to 10 M HCl. The sensitivity of the method is in the range 0.01 to 0.1 $\mu\text{g/ml}$.

Under the conditions employed, the total reagent concentration is held constant and in excess; a positive deviation from Beer's law is observed over the concentration range 10^{-6} to 10^{-5} M Eu(III). Similar behavior has also been observed for thorium and zirconium. This behavior is in contrast to the normal deviation behavior one would expect, which is a negative deviation from linearity due to an increase in the degree of dissolution of the complex with increasing metal concentration. The negative deviation is observed when the metal ion concentration is held constant and in excess, and the concentration of reagent varied.

Polarographic studies have shown that Arsenazo III is electroactive at the dropping mercury electrode (DME) and also at the pyrolytic graphite electrode (PGE). Arsenazo III in 0.1 M KCl--0.01 M HCl exhibits three cathodic waves with half-wave potentials of approximately 0.15, -0.5, and -0.8 v vs the S.C.E. for the DME. These waves are shifted approximately 0.1 v positive for the PGE. Complexing of the Arsenazo III results in a positive shift of all half-wave potentials, but not of a sufficient magnitude to be of concern to practical analytical applications.

Preliminary studies of the effect of gamma radiation on the reagent and color of the complex indicate that the method is sensitive to radiation. Under solution conditions employed in the method, radiation damage is apparent at a dose of approximately 10^4 r.

8.4 Method Evaluation

H. C. Meyer

During this reporting period, six Tramex-type solutions at full activity levels were analyzed for assorted fission products by standard radiochemical methods. The distillation method for ruthenium has shown excellent decontamination ($>5 \times 10^4$) from alpha activity, and has been accepted as a standard radiochemical method for the TRU program. The standard radiochemical methods for cerium, zirconium, and trivalent rare earths have been discarded at this time (except for glove-box operation) due to the low decontamination factors (10^2 to 10^3). The determinations of cesium and strontium are being retained, although the decontamination factors are poor (10^3 and 3×10^3 respectively), until more suitable methods are available.

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