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Consolidated Fuel Reprocessing
Program Progress Report for Period
July 1 to September 30, 1979

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**CONSOLIDATED FUEL REPROCESSING PROGRAM
PROGRESS REPORT
FOR PERIOD JULY 1 TO SEPTEMBER 30, 1979**

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FOREWORD

Effective October 1, 1978, the Department of Energy (DOE) began a transition phase to concentrate all U. S. research and development on fuel reprocessing in one major program — the Consolidated Fuel Reprocessing Program (CFRP) — under the management of the Oak Ridge National Laboratory and the Oak Ridge Operations Office. The intent of the change was to organize a single generic program which would address all fuel reprocessing development efforts. Because the future of several proposed fuel cycles is still uncertain, the resources will be concentrated to the extent possible on problems which require solutions that may be applicable in more than one of the cycles. As future directions are clarified, further moves into more specific areas are anticipated.

The CFRP in FY 1979 is organized from major segments of four programs previously underway: (1) the Advanced Fuel Recycle Program at ORNL; (2) the Converter Fuel Reprocessing Program at Savannah River Laboratory; (3) the HTGR Fuel Recycle Program, primarily at General Atomic and ORNL; and (4) the Pyrochemical and Dry Processing Methods Program at Argonne National Laboratory. Only the reprocessing components of the HTGR Fuel Recycle Program were incorporated into the CFRP. Other DOE prime contractors, along with a number of subcontractors, will participate in the program to some degree.

This CFRP progress report covers the fourth fiscal quarter of the reprocessing development program conducted at ORNL, SRL, GA, and ANL.

1. HIGHLIGHTS

1.1 Process Research and Development

B. L. Vondra

Hydrazine oxalate appears to be superior to sodium carbonate and hydrazine carbonate for solvent cleanup.

Preliminary tests showed tributyl phosphate, trihexyl phosphate, and tri(2-ethylhexyl) phosphate to have equivalent radiolytic stabilities.

Voloxidation at 600°C removed about 30% of the tritium from Elk River fuel (5% UO_2 –95% ThO_2) that had been separated from the cladding and ground to fine particle size.

Mixer-settler tests in the B-bank at Savannah River Laboratory (SRL) demonstrated highly effective separations of uranium from plutonium and thorium.

In dissolution tests with both voloxidized and untreated fast breeder fuels, plutonium losses of 0.14 to 1.0% after dissolution in 7 *M* HNO_3 were decreased to less than 0.1% by leaching for 2 h with 10 *M* HNO_3 .

Effective partial partitioning to give a uranium-plutonium product with 25 to 40% plutonium was demonstrated in glove-box plutonium flowsheet testing.

Demonstrations of the coextraction-costripping cycle and the second uranium (partial partitioning) cycle were conducted in the Solvent Extraction Test Facility (SETF) with plutonium concentrations typical of fast breeder fuels. First-cycle plutonium and uranium losses were low, and fission product decontamination factors were high. The plutonium content of the uranium-plutonium product from partial partitioning was lower than the desired 25% minimum value.

The solubility constant for thorium peroxide is almost an order of magnitude higher than that for uranium; coprecipitation is only effective at nitric acid concentrations of 1 *M* or less. Coprecipitated U-Th peroxide was successfully fabricated into pellets.

An improved gas train apparatus for the analysis of ^{14}C in gas samples was constructed and tested.

1.2 Engineering Research

W. S. Groenier

Operations of the full-scale experimental voloxidizer (FSEV) system continued with tests to address the problems of solids spilling into the inlet breaching section and the operation of the off-gas filter. Improvements were made in the Bristol controller system. Experiments were performed using the small voloxidizer to test a mathematical model for gas-phase heat transport in rotary kilns. This work is continuing. It was noted in the solid sorbent evaluation study for voloxidizer off-gases that Linde type 3A molecular sieves (the preferred sorbent) retain different amounts of iodine, depending on the type of binder used during manufacture. A rotary kiln seal evaluation study has begun.

In the dissolution task, the rotary dissolver erosion-corrosion test has been delayed again by failure of the drum support hardware. Stainless-steel ball bearings are being installed to replace the Graphitar bearings that will not withstand the environment within the steam chest. Flow modeling studies are continuing with the use of two computer programs; MATL.BAL is a stagewise material balance program, and a new code has been developed to predict changes in the dissolver liquid product concentration and flow rate that result from a step change in acid feed characteristics.

Pumping characteristics of a particular design of fluidic diode have been measured for a variety of conditions up to a flow rate for water of greater than 4 gpm at a pumping head of 42 ft. The motivating pressure was 28 psig for this case.

Fabrication of the second (12-cm) annular centrifugal contactor sized to process 0.5 t/d of fast breeder reactor fuel is almost complete. Models and correlations developed using the first (9-cm) contactor were extended by using data from a 25-cm contactor. Design has begun on a smaller (4-cm) contactor for the study of the effect of third phase formation on contactor operation. The MATEX computer code is being developed to predict steady-state concentrations for multistaged solvent extraction systems as an adjunct to the existing SEPHIS code. The new code is being used to examine the 200-series HEF stripping columns and to develop a nonreductive partitioning flowsheet. The DISCOE code has been developed to generate distribution coefficient tables and plots and is being described in a topical report. Using the Robatel centrifugal contactor installed in the General Atomic (GA) pilot plant, experimental testing was completed to determine the suitability of this contactor for uranium extraction and for scrubbing ^{95}Zr fission products. A functional check and calibration of instrumentation and the process control computer system were completed in the integrated HTGR off-gas treatment system at GA.

Modifications are underway to rework the intermediate section of the single-column selective absorption unit to allow a better match with the absorber section. Higher solvent and gas flow rates will be possible with this improvement. The experimental apparatus to measure the effects of various impurities on the fluorocarbon solvent is ready to operate. A thermodynamic consistency test procedure has been developed for use in evaluating experimental data. In the solid sorbent evaluation study, benchmark tests are underway to measure the capacity of silver mordenite for elemental iodine. Flakes of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ have been evaluated for the ^{14}C removal process. As with pelleted material, the flakes undergo a preconditioning step during which the removal is poor. Conversions in excess of 99% were measured in runs where the mass-transfer zone was approximately 2 in.

1.3 Engineering Systems

M. J. Feldman

Relative capital and operating costs of reprocessing facilities for nuclear fuels were determined for a variety of fuel types, processing modes, and capacities as a part of the Nonproliferation Alternative Systems Assessment Program.

Experiments using either a plasma torch or a laser have shown promise as a means of disassembly for fuel assemblies.

Rates to equilibrium from start-up conditions and from process flow rate changes have been determined for the rotary dissolver. These were based on a 32-h continuous run using iron rods as a substitute for fuel rods.

The design is complete and the contractor has started work on the General Plant Facility portion of the Integrated Equipment Test facility. Also, progress is being made on

design of the Integrated Process Demonstration and Remote Operation and Maintenance Demonstration portions.

The HEF basic building design has been revised to reflect the center-aisle maintenance concept. This arrangement will be used in the Conceptual Design Report for this facility. Process equipment layout studies for the HEF are complete, and equipment sizing and arrangement studies have commenced.

1.4 Technical Support

A significant reduction in energy consumption was accomplished by permanently reducing power consumption for lighting the building by 54 kW, with an additional 70 kW of lighting now routinely turned off at night. Currently, 14 kW of lighting burns continuously.

Accomplishments in the safeguards task included completion of the six safeguards-related criteria documents for the HEF and the completion of the first test of the dynamic material balancing experiment during real-time operation of the prototype dissolver system.

While calculating the results of previous FTR fuel pin experiments, an error was discovered in the cross-sectional data used with the KENO-IV codes. The error was corrected and other users of the codes were notified.

A commercially available flow monitor was tested and found to have a precision of 5% in the flow range of interest in the HEF. This is much better than any of the instruments previously tested.

1.5 HTGR Fuel Reprocessing

B. L. Vondra

A report was prepared to document an update of a prior HTGR commercial recycle plant design basis and cost estimate. Resulting direct construction cost estimates, equipment lists, and cell space requirements are included in the report. A user's manual for the computerized cost data base has been drafted and is being published.

A Joint Prototype Head-End Facility (JPHF) is in the early stages of conceptual design. This will be a cold, remotely maintainable, full-size facility. It will be cooperatively designed, built, and operated by the United States and the Federal Republic of Germany, using both U.S. and FRG reference fuel types.

Hot-cell studies with fuel test element (FTE) 16 have been completed; the results of the studies are being compiled for publication. This test element contained fuel particles of the Fort St. Vrain type, and was irradiated in the Peach Bottom Reactor for 512 effective full power days.

The long-term fission product volatility experiment has indicated that semivolatile fission products will accumulate on surfaces maintained below 500°C.

1.6 Pyrochemical and Dry Processing Methods

W. S. Groenier

Official notice has been received that the Pyrochemical and Dry Processing Methods (PDPM) Program is to be terminated effective September 30, 1979. All contractors have

been notified and instructed to complete close-out activities and to prepare draft topical reports.

The turntable transport process (TTP) design for uranium-plutonium salt is complete. To ensure proliferation resistance of the process, vessel heels will be engineered into the process so that even if a decontaminated alloy were introduced into the acceptor vessel, the resulting radiation level would meet proliferation requirements. The second generation computer model (SALT-II) of the salt transport process has been completed. In proof-of-principle studies, an experiment representing the FP-3/donor alloy segment of the salt transport process yielded results for uranium and plutonium distribution coefficients which agreed with estimated values. In a similar experiment representing the uranium-plutonium/donor alloy, the experimental values were different from the estimated values; however, appropriate separations were indicated. Differential thermal analysis (DTA) measurements are being made on the uranium-copper-magnesium system, with the goal of producing a phase diagram. These measurements will be continued by the Colorado School of Mines under the graduate studies program.

Electron microprobe studies for the thorium-uranium salt transport system indicated the existence of ThCd_{11} , ThCd_6 , and $\text{ThCd}_{3.4}$ as intermediate phases in the thorium-cadmium system. Based on the available information, a preliminary ternary phase diagram of the cadmium-magnesium-thorium system has been drawn.

Only about a 10% reduction of thorium oxide by calcium metal in a molten salt-molten metal system was achieved in a factorial experiment of nine reductions. No explanation for the low reduction has been offered. Decomposition-potential measurements of CaO in fluoride salts confirmed previous assignments (of CaO decomposition potentials) in the CaCl_2 - CaF_2 system. The separation of the CaO decomposition potential from that of CaCl_2 is possible by using a carbon anode, despite the fact that this decomposition potential is higher than anticipated based on free energy of formation data.

It has been determined that alteration of the volatilization or condensation temperatures in the chloride volatility process could lead to the separation of fissile material from fertile material. However, there would be fission products associated with the fissile material to offer diversion resistance.

Tests on urania and thoria in the molten salt processes applied to nuclear fuels demonstrated that the rate of dissolution in $\text{LiCl}/\text{AlCl}_3$ at a temperature of 610°C is rapid and will meet process requirements.

Thermodynamic analysis of the phase relationships in the uranium-plutonium-zinc system is continuing. A ternary phase diagram for this system has been developed. Differential thermal analysis measurements are being used to confirm the theoretical phase diagram.

2. PROCESS RESEARCH AND DEVELOPMENT

B. L. Vondra

The research and development activities reported in this section provide processing parameters and recommend materials of construction for both the Integrated Equipment Test (IET) and the Hot Experimental Facility (HEF) design efforts; new process options (or steps) are also being explored. An emphasis is placed on solution properties in dissolution and solvent extraction steps, and attention is being given to several aspects of plutonium chemistry and solvent properties. Hot-cell activities involve examining the voloxidation and dissolution properties of a variety of LWR fast breeder and thorium fuels. Testing of the partial partitioning of solvent extraction flowsheets is proceeding at ORNL in glove-box mixer-settler equipment and in the Solvent Extraction Test Facility (SETF), which has an irradiated fuel capacity in the kilogram-per-day range. Thorium fuels flowsheet testing is being carried out in mixer-settlers at Savannah River Laboratory (SRL); the installation of a glove-box pulsed-column facility for flowsheet testing is nearly complete. The product conversion program is establishing methods for converting mixed-oxide nitrate solutions to fabricable oxide powders. New analytical methods for process control are being developed and adapted where possible for in-line operation. A materials compatibility program is identifying suitable materials of construction for the IET and the HEF.

2.1 Laboratory Development (ORNL)

J. C. Mailen

2.1.1 Pu(IV) polymer reaction in aqueous solutions

H. A. Friedman, L. M. Toth, and M. M. Osborne

An improved method of determining free acid values in Pu(IV) stock solutions has been established. This method was recently used as an aid in determining the source of the discrepancies that appeared when polymerization rates were studied using different starting solutions. We have found that the previously measured acid concentrations of stock solutions obtained from local suppliers were slightly in error; when the appropriate correction was applied to the previously reported rates, it had the effect of changing the HNO_3 concentrations by $-0.02\text{ }N$ (e.g., the value of $0.13\text{ }N$ in Fig. 2.5 of Ref. 1 is really $0.11\text{ }N$). Furthermore, when corroboration runs were made using other sources of Pu(IV), for example, solutions made by dissolving $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ crystals in dilute acid solution, the rates of Pu(IV) polymer formation agree with those of the corrected $0.05\text{ }M$ Pu(IV) reference data set. It is apparent that (1) a reliable procedure for measuring Pu(IV) polymerization rates has now been established; and (2) with it, a reproducible set of polymerization data for $0.05\text{ }M$ plutonium solutions has resulted.

Our attention has now turned to a polymerization study of Pu(IV) solutions that are more concentrated than those previously used. These solutions must be prepared by dissolution of stock crystalline material of very low acid content; otherwise, the acid content of

the final solution would be too high for a practical test. We are presently deacidifying $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ crystals by prolonged N_2 sparging at 40°C .

2.1.2 Plutonium reductive stripping studies

M. H. Lloyd and S. E. North

Studies of plutonium reductive stripping behavior using ascorbic acid, hydroxylamine nitrate (HAN), and ascorbic acid-HAN mixtures as reductants at 25 and 50°C have continued. Particular attention has been given to dibutyl phosphate (DBP)-complexed plutonium, because previous studies have shown that this species cannot be effectively reduced and stripped with HAN at 25°C .

In these experiments, the 30% TBP solvent, which contained 0.005 M DBP and 1.5 g/liter of plutonium, was batch-contacted with seven successive equal volumes of strip solutions. The time of each contact was 2 min.

Both TBP- and DBP-complexed plutonium were effectively reduced and stripped by ascorbic acid at 25°C when the HNO_3 concentration of the strip solution was in the range of 0.1 to 1.0 M . At 50°C , effective stripping was not obtained above 0.5 M HNO_3 . The upper acid limit is primarily due to the reoxidation of $\text{Pu}(\text{III})$ during the 2-min mixing time. This appears to result from the oxidation of ascorbic acid to dehydroascorbic acid. The lower HNO_3 concentration limit is dictated by the formation of solids and emulsions when DBP is present. This occurs at about 0.1 M HNO_3 when either ascorbic acid or HAN is used as the reductant, at least for the DBP concentration (0.005 M) used in these experiments.

Increasing the temperature from 25 to 50°C results in improved reduction of DBP-complexed plutonium by HAN, particularly at low acid concentrations; however, plutonium losses are still greater (by a factor of 100 or more) than for comparable experiments with ascorbic acid.

Stripping experiments were also performed using mixed ascorbic acid and HAN as reductants at 25 and 50°C . At 25°C , effective reduction of DBP-complexed plutonium was again obtained at strip acid concentrations of about 0.1 M to 1.0 M ; satisfactory reduction was not obtained at 1.5 M HNO_3 . At 50°C , plutonium stripping was most effective when the HNO_3 concentration was in the range of 0.05 to 0.5 M . With this condition, more than 99.99% of the plutonium was stripped in two or three contacts. Slight emulsions were observed at 0.05 M HNO_3 , and solids formation occurred at 0.02 M HNO_3 .

Similar experiments are in progress with solvent that contains both uranium and plutonium. It is expected that the adverse effects of DBP on plutonium stripping will be greatly decreased, since DBP is preferentially complexed by uranium at high U-Pu ratios.

2.1.3 Plutonium-uranium-thorium coextraction

J. B. Knauer and M. H. Lloyd

The process of normalizing plutonium-uranium-thorium distribution coefficient data collected last year was initiated during this report period. This process involves the use of computer programs that incorporate simple regression techniques to fit the experimental data to mathematical expressions, thereby eliminating data scatter. This procedure worked very well in eliminating random scatter from the data. However, in cases where distribution data were not consistent with the majority of data in a given series, it was necessary to repeat the experiments.

Experiments have been repeated at 25°C to collect plutonium-uranium-thorium distribution coefficients from aqueous feed solutions containing 1 g/liter plutonium; the acid concentration varied from 0.1 to 4.5 M HNO₃. The uranium concentrations were varied at 0, 15, 25, 50, and 100 g/liter, and the thorium concentration was varied at intervals of 15, 50, 100, and 200 g/liter at each uranium concentration. The uranium and thorium distribution coefficients obtained in these experiments eliminated the discrepancies observed in the original data, and very good overall agreement was obtained.

This was not the case, however, for plutonium distribution coefficient data obtained in the two sets of experiments. It was observed that the plutonium distribution coefficients obtained in the repeated experiments were from 40 to 50% lower than the values obtained originally. Several possibilities were considered and checked to explain this difference. It was found that good agreement between the two sets of plutonium distribution coefficients resulted when the gross alpha values obtained for the aqueous feed and raffinate solutions in the repeated experiments were corrected for ²⁴¹Am growth. The corrected values eliminated most of the inconsistencies seen in the original data, with good overall agreement at each uranium concentration studied, except at 50 g/liter. At this concentration, a difference of 10 to 15% between the two sets of experimental data still remained following the correction for ²⁴¹Am growth. An explanation for this difference has not been found.

2.1.4 Fission product chemistry

L. Maya

Work on the chemistry of extractable ruthenium in the nitric acid-tributyl phosphate-dodecane system was completed. A summary of the more pertinent results of this study is given below.

Fission product ruthenium is present in the form of nitro and nitrate complexes of nitrosyl ruthenium in solutions resulting from the dissolution of spent nuclear fuel. A fraction of the ruthenium, mostly higher nitrate complexes, is extracted into the organic solvent phase in the Purex process. In stripping tests, a ruthenium component was found in the solvent phase that could not be transferred to the aqueous phase. Experiments were performed to determine whether this component was a highly extractable species originally present in the aqueous phase or if it was the product of a reaction between extracted species and the solvent. A chromatographic procedure revealed no species in the aqueous phase more extractable than the tetranitrate complex. In other experiments, evidence was found for a reversible reaction in the solvent phase that yields a species not readily transferred to the aqueous phase. The equilibrium concentration of this species is dependent on the temperature and the tributyl phosphate activity. This complex apparently results from the replacement of aquo ligands by tributyl phosphate in the extracted species.

2.1.5 Transfer kinetics

O. K. Tallent, K. E. Dodson, and J. C. Mailen

Tests using a Lewis-cell phase contactor have been conducted to examine the effect of HAN on the transfer rate of Pu(IV) from 30% TBP to 0.25 M HNO₃. The effect of HAN on the transfer rate was the same, within experimental accuracy, as that obtained by the same concentration of NaNO₃ (0.25 to 1 M HAN or NaNO₃), indicating that HAN does not participate as a reductant in the initial transfer of plutonium from the organic to the aqueous phase. Thus, the mechanism for plutonium reductive stripping with HAN is the

transfer of Pu(IV) from the organic to the aqueous phase, followed by the reduction of Pu(IV) to Pu(III) with HAN in the aqueous phase. Identification of the reductive stripping mechanism makes it possible to use existing organic-to-aqueous transfer rate data for Pu(IV) and existing Pu(IV) reduction rate data in the aqueous phase to calculate the overall reductive stripping kinetics for a two-phase system.

2.1.6 Solvent cleanup

O. K. Tallent and L. M. Gray

A new solvent cleanup method that makes use of hydrazine oxalate as a wash solution has shown considerable promise.

Solvents that have been tested include unirradiated solvents that have been degraded by a standard chemical treatment, and irradiated solvents. Unirradiated solvents were prepared by refluxing with 3 M HNO₃ containing zirconium or uranium, followed by washing with very dilute HNO₃. The solvents typically contained about 1×10^{-3} M Zr or about 8×10^{-3} M U, about 2×10^{-2} M DBP, less than 0.01 M H⁺ or about 8×10^{-3} M DBP, and less than 0.01 M H⁺. The irradiated solvent sample was obtained from the Solvent Extraction Test Facility following a processing campaign with irradiated LWR fuels. The solvent contained 1×10^5 alpha counts min⁻¹ ml⁻¹ (mainly ²³⁹Pu), 5×10^4 gamma counts min⁻¹ ml⁻¹ (mainly ¹⁰⁶Ru), 0.15 mg U per ml solution, and less than 0.01 M HNO₃. In all tests the solvent was 30% TBP in normal paraffin hydrocarbon diluent.

The hydrazine oxalate wash procedure is the same as past wash procedures except that hydrazine oxalate is used instead of hydrazine carbonate or sodium carbonate. The potential advantages of the new wash method are listed below.

1. Sodium nitrate produced in the sodium carbonate wash method, which must be stored as long-term waste, is not produced using hydrazine oxalate.
2. Hydrazine oxalate solutions are easier to prepare and are more stable than are hydrazine carbonate solutions.
3. Hydrazine oxalate solutions appear to be at least as effective in cleaning up solvents as hydrazine carbonate or sodium carbonate solutions. In tests where standard degraded solvent samples were washed with equal volumes of 0.25 M hydrazine oxalate solution, it was found that solvent uranium retentions decreased from about 2000 µg/ml to about 0.1 µg/ml; zirconium retentions decreased from about 110 µg/ml to about 10 µg/ml. Dibutyl phosphate decontamination factors of about 300 were achieved. With irradiated SETF solvents, the gross alpha activity (mainly ²³⁹Pu) decreased from about 1×10^5 to about 1×10^3 alpha counts min⁻¹ ml⁻¹. These retentions were generally lower than retentions obtained in similar tests using hydrazine carbonate or sodium carbonate washes.
4. Precipitation, gassing, interfacial "crud" formation, and slow phase separations are all problems encountered using hydrazine or sodium carbonate wash solutions. These problems have not been observed using the hydrazine oxalate wash method. The destruction of hydrazine oxalate in spent wash solutions is not expected to present a serious problem. Various oxidation methods for destroying the salt can be devised. One method that showed promise based on a preliminary test involved adding hydrogen peroxide to destroy both the hydrazine and the oxalate components of the salt.² The hydrazine component is destroyed at a pH greater than 4, after which dilute nitric acid is added to

catalyze the oxidation of the oxalate component by the peroxide. A potential advantage of this method is that little or no hydrazoic acid (or azides) is produced when hydrazine is destroyed by hydrogen peroxide.

2.1.7 Solvent scrubbing kinetics

J. C. Mailen, D. E. Horner, and S. E. Dorris

The kinetics for scrubbing DBP, uranium-DBP, and zirconium-DBP from simulated degraded solvents are being determined with various aqueous solutions. The data are analyzed assuming pseudo-first-order kinetics for the transfer.

Rising- and/or falling-drop tests have shown much more rapid transfer rates than those obtained previously using the Lewis cell, which leads to the conclusion that the Lewis cell tests were diffusion-controlled. Approximate equivalent rate constants were obtained in both the rising-drop tests and the falling-drop tests, indicating that, under drop conditions, the transfer is not diffusion-controlled. All future tests will use the drop system to approximate (as closely as possible) an operating process.

Preliminary results from uranium-DBP complex scrubbing indicate that:

1. The presence of nitrate has little effect on solvent scrubbing kinetics with sodium carbonate solutions.
2. The rate of scrubbing decreases as the sodium carbonate is converted to sodium nitrate by reaction with HNO_3 in the solvent.
3. The scrubbing rate with 0.25 *M* hydrazine oxalate at pH 8 is comparable to the scrubbing rate with 0.25 *M* Na_2CO_3 .
4. When the pH of 0.25 *M* hydrazine oxalate is reduced from 8 to 7, the scrubbing rate decreases by about a factor of 3.
5. In some tests, precipitates and interfacial cruds were observed. However, the uranium and DBP concentrations in these particular tests were much higher than would be expected in actual processes.

We are currently examining the behavior of hydrazine carbonate scrubbing solutions and the removal of the zirconium-DBP complex by various scrubbing solutions.

2.1.8 Evaluation of alternate extractants

W. D. Arnold and F. I. Case

Studies of alternate extractants to TBP have continued, with emphasis on tri-*n*-hexyl phosphate (THP) and tri(2-ethylhexyl) phosphate (TEHP). The extraction properties of these compounds are similar to those of TBP; initial evaluations have indicated that they have potential process advantages over TBP, including much lower aqueous-phase solubility and a lower tendency toward third-phase and precipitate formation. The stability of TEHP to hydrolytic degradation is much greater than that of the other two extractants.

Radiolytic stability test. Tests were conducted to a total dose of 4 Wh/liter in a ^{60}Co source to compare the radiolytic stability of 1.09 *M* trialkyl phosphate solutions in normal dodecane (NDD) in contact with 1 *M* HNO_3 . The results of these tests (Fig. 2.1) indicate the same degradation rate for all three trialkyl phosphates, as measured by the formation

Fig. 2.1. Radiolytic stability tests – dialkyl phosphoric concentrations produced by ^{60}Co irradiation of 1.09 M trialkyl phosphate-dodecane solutions in contact with 1 M HNO_3 at about 23°C .

rates of the corresponding dialkyl phosphoric acids. About 3×10^{-4} moles of the dialkyl phosphoric acids formed per liter of solvent per watt-hour per liter dose up to 1.5 Wh/liter. The formation rate decreased at higher doses.

The ^{60}Co source used in the radiolytic stability tests had a source strength of 3.5 W/liter (calibrated with ceric sulfate solution). The test solutions (5 ml of 1.09 M trialkyl phosphate in NDD and 5 ml of 1 M HNO_3) were equilibrated in a glass vial before irradiation. The phases were equilibrated again at the end of the irradiation period; the dialkyl phosphoric acid concentration in the organic phase was then determined by measuring the ^{95}Zr extraction coefficient.

Physical properties. The density, viscosity, and surface tension of the three extractants in NDD were measured as a function of extractant concentration. The density and viscosity of the solvents increased with increasing extractant concentration, but the interfacial tension decreased slightly. The viscosity was slightly higher after the extractant samples were equilibrated with 1 M HNO_3 . The magnitude of all three properties of the solvents was $\text{TEHP} > \text{THP} > \text{TBP}$.

2.1.9 Solution instability and solids formation

R. L. Fellows, D. H. Newman, and M. H. Lloyd

The study of precipitate formation from synthetic fuel reprocessing solution has shifted from reflux temperatures to lower temperature studies in nitric acid. As the scoping studies suggested, thorium molybdate exhibits a negative temperature coefficient of solubility, that is, thorium molybdate becomes less soluble with increasing temperature. The solubilities at 70°C and at nitric acid reflux temperatures are presented in Fig. 2.2 for solutions with thorium contents in the range of 100 to 200 g/liter. Thorium molybdate's negative temperature coefficient, like those of zirconium, uranium, and probably plutonium

Fig. 2.2. Molybdenum solubility in nitric acid containing thorium. Solid line at 100 g/liter thorium, and broken line at 200 g/liter thorium.

molybdates, can be potentially troublesome in certain types of process equipment by causing a deposition of the precipitates on heat transfer surfaces.

When nitric acid solutions containing thorium are supersaturated, precipitation does not begin immediately, but rather follows a latent or induction period. The length of the induction period is related to the degree of supersaturation of the solution. The most significant behavior is a large increase of the induction time with decreasing temperature. This relationship is also becoming evident in lower temperature experiments on zirconium and uranium molybdates.

The plutonium carrying behavior of thorium molybdate precipitates has been studied in 0.7 M HNO₃ at 70°C. At solution concentrations of 38 and 45 g/liter of plutonium and thorium respectively (with 1 g/liter molybdenum), the precipitate which formed contained 16% plutonium based on the total metal content. This is higher than the carrying behavior of zirconium molybdate measured previously.

2.1.10 Nitrogen compound chemistry

F. J. Smith, M. R. Bennett, G. M. Brown, and L. Maya

The N₂H₄-CO₂-H₂O system is being investigated in support of solvent cleanup development studies. Recently, hydrazine carbazate, (NH₂NHCOO)N₂H₅, was isolated by precipitation (with CO₂ at 0°C) from a concentrated hydrazine solution. Carbazic acid, NH₂NHCOOH, was obtained by drying the hydrazine carbazate over sulfuric acid. The spectra of these solid compounds are being used to verify, if possible, the presence of hydrazine carbazate or carbazic acid in solution.

In studies of the reaction of hydroxylamine nitrate (HAN) with nitric acid in the absence of air, several tests at room temperature were completed over a HAN concentration range of 0.52 to 2.6 *M*. In all of these tests, the product gas contained both N_2O and N_2 , the concentration of N_2 being about 20 vol %. In each case, 0.5 millimoles of gas ($N_2O + N_2$) per millimole of HAN consumed were evolved.

It was previously reported that HAN reacts spontaneously with 3 *M* HNO_3 at 25°C when the HAN concentration is about 0.015 *M* or less; however, above that concentration, there is an induction period which increases with increasing HAN concentration up to about 0.035 *M* and above which no reaction was observed to occur even after 96 h. An attempt to demonstrate that some intermediate compound was being formed during these induction periods, by running successive spectral scans during one of them, gave negative results. Other tests indicated that the induction period is not due to impurities in the HAN and the HNO_3 .

The kinetics of the reaction of HNO_2 with NH_3OH^+ in 1 to 3 *M* HNO_3 and at variable ionic strengths was examined by Kelmers et al.³ The reaction proceeds according to

The reported rate law showed a fractional dependence on the concentration of NH_3OH^+ , which is not consistent with the first-order dependence found by others.⁴ The kinetics of this reaction has been reinvestigated at constant ionic strength ($\mu = 2.0$ *M*), using $LiNO_3$ to replace HNO_3 in order to determine if HNO_3 participates in the reaction.

The rate of disappearance of HNO_2 was measured at 25°C in a stopped-flow kinetic spectrophotometer. Changes in transmitted light were converted to changes in absorbance, which were directly proportional to the concentration of HNO_2 . All rate constants were determined with the concentrations of HNO_3 and NH_3OH^+ in excess (tenfold or greater) of the HNO_2 concentration. These tests showed the reaction to be first-order in both the HNO_2 and the NH_3OH^+ concentrations.

The acid dependence of the second-order rate coefficient, k' ,

$$-\frac{d}{dt} [HNO_2] = k' [HNO_2] [NH_3OH^+], \quad (2.2)$$

$$k' = \frac{a[H^+]}{1 + b[H^+]}, \quad (2.3)$$

where a and b are, respectively, $14 M^{-2} s^{-1}$ and $0.51 M^{-1}$. The anomalous rate law derived from the data of Kelmers et al.³ is apparently due to the lack of control of the ionic strength of the solution. Also, there is no kinetic evidence for participation of nitric acid in the reaction.

2.2 Laboratory Development (General Atomic Company)

R. D. Zimmerman and G. E. Benedict

2.2.1 Vertical centrifuge testing

L. J. Olguin

A Sharples P-850 Super-D-Canter centrifuge has been installed in the General Atomic Company reprocessing pilot plant as part of the prototype-scale, dissolver-centrifuge system.

The centrifuge is designed for continuous mode operation and employs a unique, vertical solid-bowl configuration, which is well suited for adaptation to remote hot-cell operation and maintenance.

The results of 16 centrifuge tests are given in Table 2.1. The solids-liquid separation efficiency of the centrifuge was evaluated throughout a range of operating conditions which varied the slurry feed rate, the centrifuge g-force, the solids concentration, the solids density, and the liquid density. The dissolver slurries consisted of glass beads or diatomite dispersed in water or 7.4 M $\text{Ca}(\text{NO}_3)_2$ solution. Both types of solids tested ranged in diameter from 0 to 44 μ . Within the range of operating conditions tested, it was determined that liquid density and centrifuge g-force each have a prominent effect, and the solids content of the feed has a smaller effect on the separation efficiency. As expected, it appears from these tests that optimum solids-liquid separation will occur when the centrifuge is operating at high g-force and the slurry has a low liquid density and high solids concentration.

Table 2.1. Results and operating conditions for vertical centrifuge tests

Slurry feed rate (liters/min)	Centrifuge g-force (g's)	Solids concentration (wt %)	Particle density ^a (g/cm ³)	Liquid density ^b (g/cm ³)	Separation efficiency ^c
21.6	1080	5	1.20	1.0	0.996
14.7	1080	15	1.20	1.0	0.997
15.9	1080	5	2.45	1.0	0.995
21.6	1080	15	2.45	1.0	0.993
17.8	1080	5	1.56	1.43	0.993
12.9	1080	15	1.56	1.43	0.999
12.2	1080	5	2.45	1.43	0.984
17.7	1080	15	2.45	1.43	0.983
18.3	529	5	1.20	1.0	0.989
24.7	529	15	1.20	1.0	0.992
24.0	529	5	2.45	1.0	0.987
16.7	529	15	2.45	1.0	0.989
13.0	529	5	1.56	1.43	0.964
18.3	529	15	1.56	1.43	0.971
17.5	529	5	2.45	1.43	0.976
13.8	529	15	2.45	1.43	0.980

^aSolid particles tested were glass beads (2.45 g/cm³) and diatomite [1.20 g/cm³ in water and 1.56 g/cm³ in $\text{Ca}(\text{NO}_3)_2$]. All particles ranged in diameter from 0 to 44 μ .

^bLiquids tested consisted of water and a 7.4 M $\text{Ca}(\text{NO}_3)_2$ solution.

^cSeparation efficiency = quantity of solids removed from slurry per quantity of solids fed to centrifuge.

2.2.2 Dissolution tests

H. H. Yip

In earlier work, ThO_2 dissolution of ThO_2 kernels in boiling Thorex solution was much slower in a scaled-up unit than in a small unit. This was attributed to poor dispersion of the solids in the larger unit, thus reducing the available surface area for liquid-solid

contact. Methods for improving solids dispersion are being studied in a 0.1-m glass dissolver with a 2-liter capacity. Tests using a pump recirculation loop to disperse the solids indicated the optimum recirculation rate to be about 3% of the reactor liquid volume per minute.⁵

With the minimum required recirculation rate established, two liquid circulation designs more suitable for hot-cell operation were evaluated. The first design, an internal thermosiphon recirculator, was tested with ThO_2 and water; however, since the recirculation flow through the bed was negligible, this concept was abandoned. Better results were obtained with an internal airlift recirculator consisting of three pipes with no moving parts. The solution is airlifted to a height that will give enough hydraulic head to overcome bed resistance. The recirculation rate, therefore, is a function of hydraulic head, the drain pipe diameter, and the airlifting rate.

This recirculator maintained a flow of 200 to 300 ml/min at a hydraulic head of 16 in. during the course of dissolution. Figure 2.3 shows the reduction in dissolution time required to reach the desired 1 M thorium concentration using recirculation vs no recirculation. All dissolution tests were at 40% heel operating mode. Both the airlift recirculator and the pump loop tested earlier showed a 4.3-h dissolution time, which is about half the time needed when there was no recirculation.

Fig. 2.3. Dissolution-time plot. (Courtesy General Atomic Company)

2.2.3 Effect of uranium and zirconium on TBP hydrolysis

R. G. Wilbourn

Earlier tests showed that the presence of thorium greatly increases the TBP hydrolysis rate.⁶ Recent tests showed that uranium and particularly zirconium have the same effect. The analytical procedure used in all cases is based on washing the metal-MBP-DBP complexes into a sodium carbonate solution, followed by oxidation of the organic phosphate and phosphate colorimetry.

With 0.0 or 0.32 M HNO_3 present in the solvent, uranium greatly increased the TBP hydrolysis rate; however, the effect was smaller than that observed earlier with thorium (Fig. 2.4). Surprisingly, when the solvent contained 0.63 M HNO_3 , the hydrolysis rate was decreased by increasing the uranium concentration.

Fig. 2.4. Effect of uranium and acid concentration on DBP formation rate in 30% TBP. (Courtesy General Atomic Company)

The rate of hydrolysis of TBP in the presence of zirconium was considerably greater than for an equivalent thorium concentration. For example, with 0.1 M metal and 0.63 M HNO_3 in the solvent, the amount of DBP formed with zirconium present was about a factor of 10 higher than with thorium. It should be noted, however, that in the fuel reprocessing system, the concentration of zirconium will be very low compared to the thorium concentration.

2.2.4 Diluent degradation study

R. G. Wilbourn

Identifying a dependable source of the normal paraffin hydrocarbon (NPH) diluent used in solvent extraction has been a problem. Consequently, some alternative diluents are being tested with regard to their stability to nitric acid which is important from the standpoint of fission product decontamination efficiency, process losses, and safety considerations.

An alternate process diluent, Amsco 140, was tested by refluxing it for 3 h with an aqueous phase that consisted of 0.1 *M* Th(NO₃)₄ in 1.1 or 6.5 *M* HNO₃. Little NO₂ evolution was observed, and "red-oil" did not form; therefore, the material appears to have good resistance to nitration.

In other other tests, 30% TBP solvents were prepared with NDD, NPH, and Amsco 140 diluents which had been pretreated by refluxing for 16 h with 0.1 *M* Th(NO₃)₄–1.1 *M* HNO₃ solution. The solvents were then contacted with an equal volume of 2 *M* HNO₃ that contained 300 g/liter uranium, 1 g/liter zirconium, and ⁹⁵Zr tracer. The extracts were stripped by four successive contacts with 0.01 *M* HNO₃. The amounts of the total zirconium retained by the solvents were very low ($<9 \times 10^{-4}\%$), regardless of the diluent used. Therefore, it appears that the use of Amsco 140 diluent will not significantly reduce the zirconium decontamination efficiency.

2.2.5 Steam stripping of tributyl phosphate and dibutyl phosphate from aqueous process streams

R. G. Wilbourn

Steam stripping has been used successfully to remove small residual amounts of TBP solvent from uranyl nitrate product streams. However, white waxy residues were encountered in the steam stripping of thorium-bearing process streams. These waxy residues were not characterized but apparently were due to the presence of a thorium-DBP complex that resisted steam stripping.

A simulated 1BT solution (thorium partition product) was prepared by mixing TBP and DBP with 0.16 or 0.32 *M* Th(NO₃)₄–0.4 *M* HNO₃ solution and removing the excess organic liquid after phase separation. The simulated 1BT feed was preheated and introduced at a rate of 2.5 ml/min to the top of a packed tower that was mounted over a boiler pot. Periodically, samples were taken of the boiler pot product and the distillate. The organic phosphorus compounds in the samples were converted to the phosphate ion by wet chemical oxidation with nitric and perchloric acids; the phosphate concentration was determined by colorimetry.

The data show that TBP was removed fairly effectively (74–94%) by the steam distillation treatment; however, less than 15% of the DBP was removed (Table 2.2). Increasing the thorium concentration decreased the amounts of DBP and TBP distilled.

2.2.6 Third-phase formation in the thorium-uranium-TBP system

R. G. Wilbourn

At high solvent loadings, the thorium-TBP complex exceeds its solubility limit in NPH diluent and a third phase of unknown composition forms. A series of extraction tests was

Table 2.2. Steam stripping of TBP and DBP from thorium nitrate solution

Run	Feed composition (<i>M</i>)			Fraction of total phosphate, %		Phosphorus source
	H ⁺	Th	P ($\times 10^4$)	Product	Distillate	
1	0.45	0.15	7.9	6.3	93.8	TBP
2	0.40	0.14	9.2	8.2	91.7	TBP
3	0.42	0.33	4.2	22.8	77.2	TBP
4	0.44	0.32	5.2	25.8	74.1	TBP
5	0.40	0.13	6.9	86.7	13.3	DBP
6	0.41	0.30	4.0	91.3	8.7	DBP

made to determine the relative volumes and compositions of each of the three phases for a range of thorium, uranium, and nitric acid concentrations.

The data show that the amount of heavy organic layer (third phase) formed is most strongly influenced by the amount of thorium in the original solution (Table 2.3). For given acid and thorium concentrations, the volume of the third phase decreases as the uranium concentration is increased, since the uranium is preferentially extracted by TBP.

Table 2.3 Composition of the three phases

Sample	HNO ₃ / U/Th ^a	Milliliters per phase ^b	Th (M)	U (M)	H ⁺ (M)	TBP (vol %)	Milliliters TBP per phase
1	0	49.0	0.777	0.009	0.00	0	0.00
	12	13.0	0.641	0.083	0.00	66	8.58
	232	37.0	0.074	0.028	0.00	13	4.81
2	1.5	47.0	0.581	0.029	1.34	0	0.00
	45	12.6	0.464	0.314	0.06	57	7.18
	174	39.0	0.048	0.048	0.34	21	8.19
3	3	47.0	0.418	0.045	2.94	0	0.00
	77	8.0	0.276	0.454	0.13	49	3.92
	116	46.5	0.051	0.247	0.16	27	12.56
4	0	46.0	0.884	0.090	0.00	0	0.00
	77	14.4	0.434	0.473	0.00	60	8.64
	232	38.7	0.053	0.152	0.00	19	7.35
5	0	45.5	0.812	0.047	0.00	0	0.00
	45	16.6	0.574	0.272	0.00	60	9.96
	232	37.8	0.044	0.084	0.00	17	6.43
6	3	47.5	0.363	0.024	2.72	0	0.00
	45	12.0	0.419	0.289	0.31	56	6.72
	116	40.0	0.066	0.111	0.31	23	9.20
7	3	46.5	0.309	0.004	3.02	0	0.00
	12	15.3	0.547	0.090	0.47	65	9.95
	116	37.0	0.047	0.035	0.54	21	7.77
8	1.5	47.3	0.873	0.069	1.28	0	0.00
	77	11.6	0.434	0.523	0.254	50	5.80
	232	40.0	0.037	0.196	0.006	22	8.80
9	1.5	47.8	0.845	0.038	1.54	0	0.00
	45	13.5	0.587	0.336	0.13	80	10.80
	232	38.5	0.041	0.105	0.05	17	6.55
10	1.5	47.5	0.730	0.009	1.54	0	0.00
	12	15.4	0.761	0.130	0.13	65	10.01
	232	35.3	0.037	0.025	0.13	21	7.41
11	1.5	47.5	0.644	0.060	1.24	0	0.00
	77	8.9	0.348	0.525	0.28	55	4.90
	174	43	0.053	0.225	0.97	22	9.46
12	3	48	0.877	0.075	2.98	0	0.00
	77	13.4	0.492	0.545	0.21	61	8.17
	232	39.5	0.025	0.159	0.13	20	7.90
13	3	48	0.805	0.038	2.93	0	0.00
	45	15.4	0.623	0.328	0.28	65	10.01
	232	38	0.027	0.097	0.07	16	6.08
14	3	47	0.746	0.009	3.03	0	0.00
	12	16.8	0.790	0.091	0.48	66	11.09
	232	36.2	0.028	0.022	0.05	14	5.07
15	3	47	0.642	0.066	3.03	0	0.00
	77	11.05	0.386	0.532	0.26	46	5.08
	174	41.5	0.047	0.206	0.26	19	7.89
16	3	48.2	0.583	0.038	2.97	0	0.00
	45	14.05	0.534	0.319	0.33	61	8.57
	174	38	0.035	0.105	0.33	23	8.74
17	3	48	0.494	0.010	2.90	0	0.00
	12	16.4	0.694	0.071	0.40	75	12.3
	174	36	0.041	0.028	0.33	9	3.24
18	1.5	48	0.519	0.016	1.48	0	0.00
	12	15.1	0.623	0.080	0.13	67	10.12
	174	36.7	0.055	0.028	0.06	20	7.34

^aInitial aqueous phase composition. HNO₃ is in molarity; uranium and thorium are in g/liter.

^bIn each set, upper, middle, and lower values are for the aqueous, heavy organic, and light organic phases respectively.

2.3 Savannah River Laboratory Process Development

J. D. Spencer and S. F. Peterson

2.3.1 Effect of fuel density on voloxidation of LWR fuels

J. A. Stone

Three voloxidation tests with low-density Point Beach fuel were completed and compared with tests made earlier⁷ with high-density Point Beach fuel. The tests were made in a stainless-steel laboratory-scale voloxidizer-dissolver equipped with a rotary agitator and an off-gas analysis system.⁸ On-line ⁸⁵Kr release and oxygen consumption measurements were made to monitor the course of the reaction.

Sections of rod 045 from Point Beach-1 reactor were sheared into 1.0-in. hulls to provide material for the three tests. All three sections were from near the center of the rod (Table 2.4). The density of UO₂ in the Zircaloy-clad fuel was 94% of theoretical; initial ²³⁵U concentration was 3.03 wt %. Fuel burnup, which was determined by subsequent dissolution and analysis of the voloxidized fuel, was 28,000 MWd/MTU.

Table 2.4 also summarizes the conditions for the voloxidation tests. Base conditions (test 22) were 1.0-in. hulls, 20% oxygen, 490°C, and agitation. Because oxygen concentration was found to have a large effect on the voloxidation rate in the earlier tests with high-density Point Beach fuel, 100% oxygen was used in test 23. Test 24 was at base conditions except that the fuel was separated mechanically from the hulls.

In each test, the fuel disintegrated into a fine powder, with particle sizes predominantly less than 44 μ . The powder properties are almost identical with those of the voloxidized high-density fuel prepared previously.⁷

Table 2.4. Voloxidation tests with low-density Point Beach fuel^a

Test	Position, ^b in.	Hull length, in.	Oxygen concentration, %
22	90 to 105	1.0	20
23	70 to 88	1.0	100
24	70 to 105 ^c	0	20

^aTests at 490°C, with agitation.

^bDistances from bottom of rod for test charge.

^cMixture of loose UO₂ fragments not used in tests 22 and 23.

Reaction rates. Average reaction rates calculated from the slope of cumulative ⁸⁵Kr release or oxygen consumption as a function of time showed the reaction rate per unit surface area was 4.7 times faster with 100% oxygen (test 23) than with 20% oxygen (test 22). The reaction rate (g/h) for loose fragments (test 24) was about double the rate for fuel in hulls.

A comparison of the reaction rates of high- and low-density Point Beach fuel showed that the oxidation of low-density fuel was 140% faster than high-density fuel in 20% oxygen, but only 37% faster in 100% O₂.

Tritium removal in voloxidation was 99.8% or higher in all three tests (Table 2.5). About 20% of the ^{14}C and 11% of the ^{85}Kr were evolved.

Table 2.5. Tritium, ^{14}C , and ^{85}Kr evolution during voloxidation of low-density Point Beach fuel

Test	Tritium decontamination factor	Percent evolved during voloxidation		
		Tritium	^{14}C	^{85}Kr
22	435	99.8	19.4	10.3
23	765	99.9	20.2	11.5
24	4410	>99.9	23.0	11.0

2.3.2 Voloxidation of U-Pu oxide fuels J. R. Cadieux and J. A. Stone

The final voloxidation tests with mixed-oxide fuels were completed. Table 2.6 shows the voloxidation conditions for the seven experiments. The first three tests were made using fuel from the Saxton, Big Rock Point, and Quad Cities reactors. Initial PuO_2 concentrations in these fuels were, respectively, 6.6, 1.5, and 2.6% with burnups of 40,000, 25,000, and less than 9,450 MWd/t. The three fuels were fabricated by mechanical blending of the oxides and were clad in Zircaloy. Samples were oxidized at the standard process conditions of 490°C and 20% oxygen. The last four tests were made with Saxton fuel and evaluated the effects of oxygen concentration and temperature on voloxidation results.

Table 2.6. Conditions for voloxidation tests with mixed-oxide fuels

Test	Fuel	Temperature, °C	Oxygen, %
25	Saxton	490	20
26	Big Rock Point	490	20
27	Quad Cities	490	20
28	Saxton	490	100
29	Saxton	590	20
30	Saxton	490	20
31	Saxton	490	100

For these experiments, sections of the fuel rods were sheared and twelve 1.0-in. pieces were placed in the voloxidizer/dissolver. Considerable amounts of the Quad Cities fuel fragmented and separated from the hulls upon shearing.

The system reached reaction temperature (490 or 590°C) 30 to 45 min after rotary agitation and heating began. Both ^{85}Kr release and oxygen consumption were measured on-line to follow the course of the reaction.⁹

Figure 2.5 shows the relative reaction rates based on ^{85}Kr evolution, for the three different fuels at 490°C and 20% O_2 . The time required to complete the reaction increased as fuel burnup was increased. The ^{85}Kr release curves are normalized because only 5 to 16% of the total ^{85}Kr in the fuel was released during voloxidation. Oxygen uptake data gave

Fig. 2.5. Voloxidation tests of three fuel types at 490°C and 20% oxygen (tests 25, 26, and 27). (Courtesy Savannah River Laboratory)

similar rates of reaction. Test 30 with Saxton MOX at 490°C and 20% O_2 showed a steady but unusually slow reaction (Fig. 2.6). This was the first sample of fuel from a new rod. A subsequent test (31) with fuel from this rod at 490°C and 100% O_2 did not show an anomalous rate. Temperature (490 or 590°C) had no apparent effect on the rate of reaction if the data for test 25, rather than that of test 30, are accepted as representing normal behavior for the Saxton material.

In all tests, the oxidized powder separated cleanly from the hulls. Particle sizes measured by vibratory sieving showed that 88% or more of the material was less than 44 M in all tests.

Tritium release in voloxidation was highly effective in all tests with the recoveries ranging from 99.4 to greater than 99.9% but only small fractions of the ^{85}Kr and ^{129}I were released (Table 2.7).

Fig. 2.6. Effect of oxygen concentration and temperature on the voloxidation of Saxton fuel. The faster oxidation for the condition 20% O₂-490°C was obtained in test 25, the slower oxidation was in test 30 (Courtesy Savannah River Laboratory)

Table 2.7 Voloxidation test results

Test	Amount removal in voloxidation, % of total found ^a		
	¹⁴ C	⁸⁵ Kr	¹²⁹ I
25	36	8	9
26	11	9	2
27	31	<30	5
28	40	5	7
29	39	11	5
30	41	9	13
31	37	16	4

^aTritium results based on the total found in the voloxidizer off-gas and dissolver solution, others are based on total found in the voloxidizer and dissolver off-gases

2.3.3 Dissolution of voloxidized mixed-oxide fuel

J. R. Cadieux and J. A. Stone

The voloxidized Big Rock Point material (test 26 of Table 2.6) was dissolved in 5 *M* HNO₃ over a 4.5-h period. Heat was added to the system after 1.5 h of leaching, and the dissolution temperature was about 92°C over the last 2 h. The residue from this treatment was leached for 6 h at 90°C with 10 *M* HNO₃ and finally was dissolved in 13 *M* HNO₃–0.1 *M* Al³⁺–0.05 *M* HF solution.

The distribution of U, Pu, and ¹⁰⁶Ru in the various dissolver solutions is shown in Table 2.8. Essentially all of the uranium, but only 96.2% of the plutonium, was dissolved in the initial leach. The amount of residue from the initial leach was equivalent to 9.8 kg/t, which is about double the amount obtained previously with unvoloxidized Big Rock Point fuel. The 10 *M*-HNO₃ leach dissolved an additional 0.79% of the plutonium, increasing the total recovered with HNO₃ to about 98%.

Table 2.8. Uranium and plutonium distributions
in various solutions

Solution	Percent of total collected			Plutonium:uranium ratio
	Uranium	Plutonium	¹⁰⁶ Ru	
Dissolver solution and first two rinses	99.91	96.2	93.7	0.014
Two 10- <i>M</i> HNO ₃ leaches of hulls and rinses	0.09	0.97	2.2	0.154
10- <i>M</i> HNO ₃ leach of solid residue and rinse	<0.01	0.79	2.5	9.37
Fluoride leach of solid residue and rinse	<0.01	2.04	1.6	24.4

2.3.4 Solvent extraction coprocessing tests

M. C. Thompson

Five miniature mixer-settler tests were completed to evaluate different flowsheet approaches to partial partitioning. The objective was to increase the Pu/(Pu+U) concentration from its initial value of about 0.9% to about 25% in the partial partitioning system, which had 16 stages. Backscrubbing with organic was not used. Hydroxylamine nitrate (HAN) was the plutonium reductant in four of the tests and U(IV) was the reductant for the fifth test. In one of the HAN tests the strip solution also contained 0.3 *M* U(VI) to improve plutonium stripping.

Table 2.9 shows the conditions and results of the tests. The desired concentration of plutonium in the product was achieved only in the test with U(IV). However, the loss of

Table 2.9. Coprocessing tests

Test	HNO ₃ in IAS, <i>M</i>	IBX composition	IBX' composition	Flow ratio, A:O	Pu/(U+Pu) in product, %	Pu loss to uranium product, %
1	3	2.5 <i>M</i> HNO ₃ 0.10 <i>M</i> H ₂ H ₄	0.19 <i>M</i> U(IV) 2.46 <i>M</i> HNO ₃ 0.10 <i>M</i> N ₂ H ₄ Stage 15	0.15	24.2 to 25.3	~7
2	1.0	0.20 <i>M</i> HNO ₃ 0.39 <i>M</i> HAN		0.20	16.8	0.03
3	1.5	0.20 <i>M</i> HNO ₃ 0.39 <i>M</i> HAN		0.20	11.9	0.29
4	2.0	0.20 <i>M</i> HNO ₃ 0.39 <i>M</i> HAN		0.20	9.0	0.1
5	1.5	0.30 <i>M</i> U 0.29 <i>M</i> HNO ₃ 0.21 <i>M</i> HAN	10 <i>M</i> HNO ₃ Stage 12	0.20	9.4	

plutonium to the uranium product stream in this test was about 7%. The acid concentration in the system was in the range of 2.3 to 2.6 *M* and, at this high acidity, plutonium was not removed effectively from the solvent in the lower stages (Fig. 2.7). Apparently, there was some plutonium reoxidation since the distribution coefficient for plutonium increased to 0.86 in stage 2, indicating the presence of Pu(IV).

Fig. 2.7. Plutonium and HNO₃ profiles in partial partitioning (tests 1 and 5). (Courtesy Savannah River Laboratory)

Much more effective plutonium recoveries were obtained in the tests with HAN reductant; however, steady-state operation may not have been obtained in these tests. Surprisingly, the Pu:U ratio in the product stream decreased when the HNO_3 concentration of the scrub solution (1AS) in the extraction-scrub system was increased. This is opposite to the effect expected since the higher acid concentration should have resulted in more transfer of acid to the partial partitioning system and thus more effective uranium salting into the solvent.

Future tests will concentrate on improving the U(IV) flowsheet; a lower acid concentration will be used for stripping.

2.3.5 Low decontamination flowsheet

M. C. Thompson

Studies using miniature mixer-settlers investigated a flowsheet in which a significant portion of the fission products are extracted and stripped with the plutonium.

In the initial tests, the feed contained uranium, natural zirconium, and 2.5 M HNO_3 . Plutonium was not present, but the solvent was passed into a partial partitioning system which was operated in a manner similar to that described in Sect. 2.3.4. Zirconium was analyzed spectrophotometrically as the xylenol orange complex. The zirconium concentration in the plutonium product (1BP) varied depending on the level of saturation of the organic phase with uranium in the extraction system. The amount of zirconium in the 1BP varied from over 99% at 56% saturation to 82% at 66% saturation. Concentration profiles of the extraction system showed that zirconium and nitric acid refluxed to concentrations much higher than in the feed. Increasing the level of uranium loading caused the acid and zirconium to reflux to a greater extent, but the product contained less zirconium because less free TBP was available for retaining zirconium in the solvent phase.

In a second series of tests, the HNO_3 in the feed was varied from 0.5 to 2.0 M . The simulated feed also contained Ce, Eu, Cs, Zr, Ru, Nd, Sr, Mo, and Fe at 0.4 to 1 g/liter. An aliquot of dissolver solution from an irradiated mixed-oxide fuel dissolution test was added to the feed to facilitate determination of Ru, Ce, Eu, and Cs. In the tests with 0.5 M and 1.0 M HNO_3 in the feed, a grayish-white solid collected in the settler of stage 16. When the activity in the feed was 2 M , the solid partially dissolved, which indicates that the precipitation may be avoided by control of acidity.

The decontamination results for Ru, Eu, and Cs are shown in Fig. 2.8. The decontamination factor (DF) for ruthenium increases as the HNO_3 concentration in the feed increases, because the distribution coefficient decreases with increase in HNO_3 concentration. The DF for cesium apparently was controlled by entrainment because its distribution coefficient is low ($\sim 10^{-5}$). The data indicates very high entrainment (1.4%) with 0.5 M acid feed and 0.3 to 0.4% entrainment at higher acidity. Until the experiment can be repeated, uncertainty exists as to whether the high entrainment is characteristic of low acid feeds or if it was due to an improper adjustment of equipment during the specific test. The DF for europium is expected to be representative of rare earths in general. The magnitude of the DF for europium was lower than expected based on distribution coefficients.

2.3.6 Processing of irradiated thorium-uranium

J. B. Pickett

Testing of irradiated thorium-uranium fuel in the high-level caves began this quarter. The fuel, initially 95.4% ThO_2 —4.6% UO_2 (enriched to 93.2% ^{235}U), was irradiated in the Elk River reactor to a burnup of about 12,000 MWd/t, and has cooled for about 12 years.

Fig. 2.8. Decontamination factors for ^{137}Cs , ^{154}Eu , and ^{106}Ru in low decontamination tests. (Courtesy Savannah River Laboratory)

Three fuel rods were cut into about 30-in. lengths in the storage basin facilities at the SRP Receiving Basin for Off-Site Fuel, and then transferred to the high-level caves in SRL. The 30-in. lengths from two of the three rods were cut into about 3-in. pieces, and declad by slitting the cladding longitudinally. This technique demonstrated a 98.3% separation of the irradiated fuel from the second Elk River rod (Table 2.10). The separation with the first rod was significantly less (94.6%) because the slitter blades were misaligned. The fuel was separated by pneumatically forcing the 3-in. pieces between two opposed cutting wheels. This cut and deformed the cladding, and, in some cases, partially cracked the pellets. The cladding pieces containing fuel material were then agitated by 400 revolutions in a two-liter container. Assuming that the Elk River fuel is typical of thoria-based fuels, 1 to 2% of the fuel will probably remain with the cladding after slitting and agitation, and a Thorex leach of the cladding will be required.

The fuel was fractionated following separation from the cladding, crushed in a small hammer mill, and rescreened. In the tests using rod 1, about 73% of the fuel, before crushing, was larger than $2000\ \mu$, and 7% was smaller than $250\ \mu$. After crushing, about 5% was larger than $2000\ \mu$, and 21% was smaller than $250\ \mu$. The screened fractions from each rod were recombined and well mixed to form homogeneous feed lots for the tritium removal and dissolution tests. A description of the roasting and dissolution tests is given in Table 2.11.

Table 2.10. Separation of Elk River fuel from cladding

	Fuel separated, % of total	
	Rod 1	Rod 2
Slitting	11.8	57.6
Slitting plus agitation	94.6	98.3
Fuel remaining in cladding	5.4	1.7

Table 2.11. Roasting and dissolution tests

Run	Elk River rod	Particle size	Test description
1		Pellets	Dissolution of pellets from GE of Canada to check out equipment
3	1	<44 – >2000	First Elk River fuel dissolution test
4	1	<44 – >2000	Roasted at 600°C for 6 h in air, then dissolved
6	1	<44 – >2000	Voloxidized (run 32) at 600°C in air, then dissolved
7	2	Whole pellets	Voloxidized (run 33) at 600°C in air, then dissolved
34	2	>850 – <2000	Voloxidized at 600°C in air, then dissolved in voloxidation apparatus

All of the Elk River fuel powder samples dissolved satisfactorily (98 to 99%). Dissolution of the voloxidized whole Elk River pellets (run 7) was much poorer; only about 50% dissolved after 6 h in refluxing 13 M HNO₃–0.1 M Al(NO₃)₃–0.05 M HF.

In tests with the homogenized material that had been separated from the cladding, about 30% of the tritium was removed by voloxidation in air at 600°C (run 32). Only about 10% of the tritium was removed by the static roast at 600°C (run 4); about 1% or less of the ⁸⁵Kr was evolved in the voloxidation tests.

2.3.7 Feed clarification

M. C. Thompson and C. D. Oliver

Twenty-eight different flocculating agents were tested for their ability to clarify a simulated thorium fuel solution. The test solution contained dissolved U, Th, and Zr, and ZrO₂ solids. Two methods of timed filtration were employed in the evaluation: (1) timed vacuum filtration and (2) filtration using a Millipore Silting Index Apparatus (Millipore Corporation). Flocculants were tested at 1000, 200, 20, and 5 ppm. Results using both methods indicated that Primafloc C-3 was the best of the agents tested.

The time for vacuum filtration of 5 ml of slurry using Millipore filter HAW PO 4700 (porosity of $0.45\ \mu\text{m}$) was measured. Without flocculant added, the filtration time was 9.03 s. By adding a flocculant, this time was decreased to as low as 5.33 s. This lowest value was obtained using 1000 ppm of Primaflow C-3; the times observed using 200, 20, and 5 ppm Primaflow C-3 were 5.7, 6.4, and 6.8 s respectively. Nalco 7134, Purifloc C-43, and Betz 1160 flocculants also showed promise; the last reagent provided a filtration time of 5.9 s when used at only 5-ppm concentration.

The Millipore* Silting Index Apparatus was used to further evaluate the various flocculating agents. The apparatus applies constant pressure over a defined volume as the solution filters through a known surface area. Reduction of flow from buildup of residue is measured as a function of time. The Silting Index, S , is a dimensionless quantity characterizing this decay in flow and is expected to indicate the clarity of a solution

$$S = \frac{T_3 - 2T_2}{T_1},$$

where T_1 = time to filter volume V_1 , T_2 = time to filter volume V_2 , and T_3 = time to filter volume V_3 . The results are summarized in Table 2.12.

The Silting Index proved to be a highly unreliable measure of the filtrate clarity. The actual filtration time, T_3 , appeared to be a much more applicable measure of the flocculant effectiveness. These tests confirmed Primaflow at 1000 and 200 ppm to be the most effective. Filtration times were about 2 min compared to 6 min for the untreated solution. Filtration times for the other flocculants, including Primaflow C-3 at 20 ppm, were much longer than for the untreated solution.

Table 2.12 Silting index tests

	Concentration, ppm	Vacuum filtration time, s	Filtration time, min			
			T_1	T_2	T_3	Silting index
Primaflow ^a C 3	1000	5.33	0.078	0.740	2.192	9.8263
None		9.03	0.240	2.120	6.153	7.9191
Primaflow ^a C 3	200	5.70	0.087	0.720	2.090	7.5759
Purifloc ^a C 43	20	6.07	0.947	8.261	22.880	6.7395
Nalco ^a 7134	200	6.07	1.110	11.330	29.930	6.7099
Hercofloc ^a 1018	5	7.47	0.587	4.753	13.073	6.1016
Primaflow ^a C 3	20	6.4	1.443	11.275	30.523	5.4381
Nalco ^a 7134	1000	6.07	1.540	12.093	32.182	5.3592
Nalco ^a 7134	20	6.0	1.903	12.022	33.530	5.3071
Betz ^a 1160	5	5.9	2.173	16.319	45.042	3.1252

^aRegistered trademark

*Trademark.

2.3.8 Thorium solvent extraction

D. J. Reif

Thorium solvent extraction studies are continuing in an effort to develop technology for the recovery of Th, Pu, and U from spent thorium-based fuels. Two types of separations are being considered: (1) separation of uranium from thorium and plutonium where the uranium is recovered and the Th-Pu coproduct is stored as waste, and (2) separation of uranium and plutonium from thorium where the U-Pu and thorium are recovered.

The processes under study avoid pure fissile (^{239}Pu , ^{233}U) streams or products; ^{233}U is always diluted with ^{238}U , and ^{239}Pu is either coprocessed with thorium or uranium. Previously,⁹ a flowsheet was defined for the ^{233}U recovery process with a Th-Pu waste stream. This section summarizes the definition of the U-Pu coproduct flowsheet and the results of mixer-settler testing of both flowsheets.

The U-Pu product flowsheet includes coextraction of U, Pu, and Th (A bank), partitioning of U and Pu from Th (B bank), partial partitioning of U from Pu (C bank) and U stripping (D bank). Conditions for the flowsheet were chosen based on computer calculations using the SEPHIS-MOD4 Purex system and SEPHIS MOD-4 Thorex system codes.

Three tests of A-bank separations were made in mini-mixer-settlers with radioactive feed. The conditions for the runs are shown in Fig. 2.9. In one run, H_3PO_4 was added to the scrub stream. This resulted in the formation of gels and feed line pluggage in the contactor; the gel was probably thorium phosphate. The simulated feed contained 200 g/liter thorium, 52 g/liter uranium, and 1 g/liter plutonium in 2.5 M HNO_3 –0.3 M $\text{Al}(\text{NO}_3)_3$. Exit stream analyses showed that Pu, Th, and U losses to the A-bank waste (AW) were very low (<0.001 g/liter). In addition, the organic extract (AP) being delivered to the B-bank was consistent in concentrations of the heavy metals (in g/liter, 6.5–7.4 U, 24.6–26.9 Th, 0.10–0.12 Pu).

Fig. 2.9. A-bank decontamination. (Courtesy of Savannah River Laboratory)

The thorium was partitioned from the uranium and plutonium in the B-bank using 0.2 M HNO_3 and backscrubbing with organic. Separations were not as effective as had been predicted by the SEPHIS analysis. About 10% of the plutonium and 0.2% of the thorium followed the uranium product.

Uranium recovery process studies. In two tests of B-bank operation (partitioning of U and Pu from Th) under the conditions of the flowsheet shown in Fig. 2.10, losses of Th, Pu, and U were very low. Thus, we conclude that the Th, Pu, and U separations provided by the uranium recovery flowsheet are acceptable and that the system warrants further testing.

Fig. 2.10. B-bank uranium recovery process partition. (Courtesy of Savannah River Laboratory)

2.3.9 Pulsed-Column Facility

D. J. Reif

The design and fabrication of the 4-column laboratory-scale alpha-contained Pulsed-Column Facility (PCF) is about 65% complete. The facility will be used to develop technology for the solvent extraction processing of thorium-based power reactor fuels. The PCF is expected to be ready to begin cold tests on October 15, 1979. Hot tests should begin during March 1980.

The PCF floor-to-ceiling glove box modifications are almost complete and will be followed by the installation of equipment. The four pulsed columns, including pulsed generators and the anolyte system, have been received from the fabricator, Allied-General Nuclear Fuel Services (AGNS). Process control equipment is expected to be received soon.

A half-scale model is under construction to provide final piping detail for fabrication. The model will be used for PCF construction and operator training. A safety analysis of the PCF is proceeding concurrently with facility design.

The original facility design concept did not include reuse of recovered thorium and uranium. An evaporator has been added to allow this. All solvents will be stripped to recover the U, Pu, and Th for reuse. In addition, the facility design has been expanded to include monitoring equipment for continuous readout of exit stream density and alpha and gamma activities to determine when the process is at steady-state.

2.3.10 Thorium irradiation program

J. B. Pickett

Irradiation of a proliferation-resistant thorium-oxide-uranium oxide fuel in the SRP reactors is proposed to provide materials for the SRL chemical reprocessing studies. Approximately 9 to 13 kg of full-size pellets of several types of materials will be fabricated and loaded into Zircaloy rods by Pacific Northwest Laboratories (PNL). The fuel rods would be charged to the P Reactor at SRP for irradiation at powers simulating LWR conditions. Average exposures of about 20,000 MWd/t would be accumulated over a Mark 16B fuel cycle of about eight months. The irradiated material would be available for testing in April 1981.

The irradiation test matrix includes five to seven various material types (Table 2.13). The test fuels will be loaded into 30-in.-long Zircaloy rodlets, with three rodlets loaded into columns in modified quatrefoil assemblies; each column will contain about 300 pellets, weighing a total of 1.4 kg.

Table 2.13. Irradiation test matrix

Quatrefoil	Type	Fuel composition
I	1	100% UO_2 pellet (internal control)
	2	80% ThO_2 —20% UO_2 pellet
	3	80% ThO_2 —20% UO_2 + 0.25% CaO pellets
	4	100% ThO_2 pellet
II	1	100% UO_2 pellet (internal control)
	2	80% ThO_2 —20% UO_2 pellet
	5	100% UO_2 sol-gel hybrid pellet
III	1	100% UO_2 pellet (internal control)

The test plan has been modified to provide for up to a two-month delay in receipt of the test materials and a subsequent delay in charging the fuel columns into the reactor. To provide for these delays, the ^{235}U content was reduced from about 2.6 to about 2.1%, which was required to limit maximum heat rating. The modified test plan, which is outlined in Table 2.14, results in a lower heat rating (~ 16 kW/ft) if the materials are charged at the beginning of the cycle, or a lower total burnup if the charge is delayed two months.

Table 2.14. Modified test plan

Plan	Option	^{235}U , %	Irradiation, months	Heat rating, kW/ft		Average burnup, MWd/MTHM
				Maximum	Average	
Initial		2.6 (13.0) ^a	8	18	14	20,000
Modified	A	2.07 (11.3) ^a	8	16	~ 13	$\sim 18,000$
	B	2.07 (11.3) ^a	6	18	~ 14	15,000

^a2.07% ^{235}U in the 100% UO_2 fuels; 11.3% ^{235}U in the 80% ThO_2 —20% UO_2 fuel types.

Quatrefoil assembly and testing (J. L. Steimke). Calculations indicate that coolant flow in the modified quatrefoil assembly will be sufficient to avoid nucleate boiling. A hydraulic test assembly has been designed to measure the actual pressure drops and resulting flow in the quatrefoil assembly. A mock assembly to check out the flow monitoring equipment has been fabricated and installed in the test facility in the CMX building.

A new discharge crane cooling station used to measure how effectively the irradiated assembly can be cooled after discharge from the reactor has been designed, and fabrication was begun.

Fuel types for irradiation (J. B. Pickett). To evaluate CaO as a dissolution aid, PNL fabricated 80% ThO₂–20% UO₂ ceramic pellets containing 0, 0.33, and 0.66% CaO and shipped them to SRL for dissolution tests. It was found that the addition of CaO causes the sintered pellets to have a less uniform grain structure and grain size, with some fine cracking. The samples were considered “marginally close to commercial grade.” Testing of pellet dissolution characteristics at SRL showed that CaO improves the dissolution rate significantly. Therefore, CaO-containing pellets will be included in the test matrix.

The rate of dissolution of the pellets was appreciably increased when CaO was added. The amounts dissolved after 6 h in refluxing 13 M HNO₃–0.025 M HF–0.1 M Al(NO₃)₃ solution were 7.94, 94.1, and 98.2%, respectively, for 0, 0.33, and 0.66% CaO concentration. Other tests showed that increasing the HF concentration to 0.05 M (while keeping the Al³⁺ concentration constant) only slightly increased the dissolution rate.

2.4 Hot-Cell Development

V. C. A. Vaughen

2.4.1 Fuel procurement

J. H. Goode

A shipment of irradiated (U,Pu)C was received from the Los Alamos Scientific Laboratory (LASL). The specimens, representing a cross-section of samples in the U.S. carbide fuels program, will be used in hot-cell studies of the effects of cladding material, sodium-bonding, density, and burnup level on the conversion of carbides to oxides and their subsequent dissolution in nitric acid. Four intact specimens are being gamma-scanned prior to sectioning into smaller pieces.

2.4.2 Flowsheet parametric studies

J. H. Goode, R. G. Stacy, J. R. Travis, and C. S. Webster

The parametric voloxidation experiments with PNL-3 (U,Pu)O₂ were concluded during this quarter. Results from the earliest runs in the series indicated apparent wide variations in the tritium content of this fuel, particularly in regard to its different pellet sintering temperatures during fabrication. In December 1978, tritium concentrations in unclad, dislodged (U,Pu)O₂ ranged from $1.4 \pm 0.26 \times 10^4$ dps/g for the pellets sintered at 1525°C to as high as $4.1 \pm 1.3 \times 10^4$ dps/g for the fuel pellets sintered at 1650°C. Since that time, the total tritium recovered in the voloxidation-dissolution experiments has steadily decreased. The tritium recoveries from experiments begun as late as mid-June 1979 have dropped to an average of $7.2 \pm 1.9 \times 10^3$ dps/g for 1- and 2-in.-long segments of clad fuel sintered at either temperature.

This fuel (PNL-3) is the first prototype fast reactor fuel (natural enrichment uranium) irradiated to a high flux in a fast reactor (EBR-II) that we have studied. The quantitative spectrum of fission products from the fissioning of ²³⁹Pu is different from that from ²³⁵U and may reflect significant changes in the fuel chemical state. In addition, the low heat rating (~5 kW/ft) may also play a role in the equilibria attained.

The tritium data for the experiments are summarized in Table 2.15. The removal efficiency generally decreased with an increase in the length of time following shearing; the highest amount removed was 99.5% and the lowest was about 36%. The releases at 600°C average 99.4% for declad fuel and about $86.5 \pm 3.2\%$ for clad fuel. At 480°C, the releases average 91.2% and about $52 \pm 34\%$ respectively.

The decrease in the tritium content of the fuel with time has not been observed previously with other fuel samples and implies that at least most of the tritium in the PNL-3 fuel is in a relatively mobile form, presumably T_2 or HT.

Table 2.15. Tritium distribution for PNL-3 (U, Pu) O_2 voloxidation tests

Run ^a	Voloxidation conditions	Tritium, dis sec ⁻¹ (U+Pu) ⁻¹			Tritium removed by voloxidation, % of total found
		Voloxidizer off-gas	Dissolution	Total	
600°C					
FBR-9	Low ^b , unclad, air	1.59EO4	8.60EO1	1.60EO4	99.5
FBR-11	High ^c , unclad, air	5.04EO4	3.85EO2	5.08EO4	99.2
FBR-13	Low, 1-in., air	1.32EO4	1.97EO3	1.52EO4	87.0
FBR-14	High, 1-in., air	8.35EO3	1.54EO3	9.89EO3	84.4
FBR-15	Low, 1-in., O ₂	6.92EO3	8.49EO2	7.77EO3	89.1
FBR-18	High, 2-in., air	3.71EO3	6.32EO2	4.34EO3	85.5
FBR-20	Low, 2-in., O ₂	4.88EO3	<i>d</i>		
480°C					
FBR-10	Low, unclad, air	1.12EO4	1.13EO3	1.23EO4	90.8
FBR-12	High, unclad, air	2.94EO4	2.65EO3	3.21EO4	91.7
FBR-16	High, 2-in., air	3.74EO3	2.53EO3	6.27EO3	59.7
FBR-17	Low, 2-in., O ₂	2.43EO3	4.29EO3	6.72EO3	36.2
FBR-19	High, 1-in., air	4.97EO3	3.34EO3	8.31EO3	59.8
FBR-21	Low+High, 1-in., O ₂	6.45EO3	<i>d</i>		

^a All experiments at temperature for 3.0 hours except FBR-16 for 5.0 hours and FBR-20 for 1.5 hours.

^b Low = fuel pellets sintered at 1500 to 1540°C during fabrication.

^c High = fuel pellets sintered at 1600 to 1675°C during fabrication.

^d Analysis not complete.

Voloxidation of LWR fuels. A comparison was made of tritium recoveries during voloxidation and dissolution experiments with UO_2 fuel from three reactors: H. B. Robinson-2 (PWR, 28,000 MWd/t), Oconee-1 (PWR, 23,000 MWd/t), and Dresden-3 (BWR, 18,000 MWd/t). All tests were made at 480°C and were made with both clad (1 to 2-in. pieces) and unclad fuel.

Tritium removal in voloxidation was 99.8% or higher in all tests. The total amount of tritium in the UO_2 from the two PWR fuels was greater by a factor of 3 to 4 than that in the lower burnup BWR fuel. Determinations of the tritium content in the Zircaloy cladding

indicated that about 40% of the total tritium generated by fission in the PWRs was contained in the cladding, whereas as much as 60% of the total tritium was located in the cladding from the BWR fuel rod. This variation is probably due to the difference in linear heat ratings for the two types of reactors: about 5.5 kW/ft for the PWRs and about 13.4 kW/ft for the Dresden-3 reactor.

Carbide fuel studies. In preparation for the scouting studies with (U,Pu)C fuels during the coming fiscal year, an off-gas flow monitoring system was designed and fabricated for the detection and measurement of CO and CO₂ during the oxidation of carbides. Following shakedown and cold tests in the laboratory hood with unirradiated uranium carbide fuel, the system will be used in-line with the hot-cell voloxidation off-gas train.

Dissolution of FBR fuel. The amount of plutonium that did not dissolve in standard nitric acid leaches (7 M HNO₃) of PNL-3 fuel was lower for fuel that had been sintered at 1660°C than for fuel sintered at 1525°C (Table 2.16). This is consistent with the known fact that higher sintering temperatures increase the homogeneity of the fuel. Neither fuel was acceptably soluble, and irradiation to about 6 at.% burnup did not correct the adverse effects on solubility of nonhomogeneity of the fuel. With both fuel samples, voloxidation increased the amount of undissolved plutonium. However, in all cases, the amount of plutonium lost to the residue was decreased to less than 0.1% by a subsequent leach with 10 M HNO₃.

Table 2.16. Dissolution of PNL-3 fuel

Fuel sintering temperature, °C	Undissolved plutonium, ^a %	
	Voloxidized fuel	Nonvoloxidized fuel
1525	1.0 ± 0.3	0.65
1660	~0.5	0.14

^a Amounts dissolved after leaching in 7 M HNO₃. Subsequent leaches with 10 M HNO₃ and HNO₃-HF decreased the plutonium losses to <0.1% and <0.01 % respectively.

2.4.3 Development of a new solvent extraction computer code for flowsheet testing A. D. Mitchell

The SEPHIS program is a computer simulation of solvent extraction processes. The new program is similar to the SEPHIS program, but additional features in the new program should greatly enhance its usefulness.¹⁰ The new program will be referred to as the CONCEPT program for CONTroller-run Solvent Extraction Process Testing. A report on the CONCEPT program is being prepared.

Correlations for the distribution coefficients for the Thorex process have been added to the CONCEPT program. Testing of most portions of the program has been successfully completed and the steady-state results are identical to those produced by the SEPHIS program. This indicates that the correlations were adapted correctly.

Inserting provisions for the plutonium reduction reactions has been less successful. Small, but significant, errors in the mass balances have been encountered in testing the program. Work is continuing toward eliminating the cause of these errors, but thus far, only qualitative improvements have been made.

2.4.4 Modeling the formation of a third phase in the Thorex process

V. C. A. Vaughn and A. D. Mitchell

A correlation to model the formation of third phase was developed previously for use in the SEPHIS program.¹¹ This correlation is based on calculations for the experimental conditions used by Weinberger.¹² However, when the SEPHIS program was used to simulate Weinberger's experiments, third phase was not indicated by the program for the experiments which were used to develop the third phase correlation. In addition, during a series of batch extractions, some discrepancies were noted in which a third phase was found in the experiments, but this was not signaled by the SEPHIS program.¹³

We found that the data could be fit with a simple linear equation. Neglecting one data point, a reasonable ($\pm 1\%$) fit was given by

$$Th_o = 0.0632 + 7.05E-03 (T) - 5.67E-05 (T)^2 - 0.150H_o , \quad (2.4)$$

where

Th_o = the maximum Th concentration in the organic phase before third phase appears (M) ,

T = temperature ($^{\circ}C$) ,

H_o = nitric acid concentration in the organic phase (M) .

The data used for this correlation were in the range of $Th_o = 0.20 - 0.28 M$, $H_o = 0.0 - 0.3$, and $T = 30 - 60^{\circ}C$, 30% TBP.

2.4.5 Plutonium flowsheet tests

W. D. Bond and B. A. Hannaford

The objectives of this work are (1) to develop and test solvent extraction coprocessing flowsheets before they are tested in the Solvent Extraction Test Facility and (2) to evaluate new process options. Three 16-stage mini-mixer-settlers in alpha glove boxes comprise the principal experimental apparatus. The initial tests are being made with solutions that have a U:Pu ratio typical of LWR solutions. The flowsheet being examined includes coextraction with 30% TBP in normal paraffin hydrocarbon (NPH) diluent in the first mixer-settler bank, partial partitioning in the second bank using hydroxylamine nitrate (HAN) for reducing plutonium, and uranium stripping in the third bank.

A final uranium-only experiment, UX-3, was carried out for the purpose of demonstrating that the desired uranium concentration of 6 to 12 g/liter could be maintained in the uranium-plutonium product stream (1 BP) from the partial partitioning system; the plutonium concentration of this stream will be about 4 g/liter. The 1BP stream was continuously monitored by two in-line monitors: a Beckman spectrophotometer and a Mettler DMA45 densitometer. At 300 min run time, a fairly steady concentration of 8 g/liter of uranium

(equivalent to ~33% plutonium) was obtained; the 1BS organic backscrub rate was then increased by about 5% to examine the sensitivity of the system to small flow rate changes. The uranium concentration reached the value of approximately 6 g/liter of uranium, remaining at this concentration for the final 120 min of the run.

Following an initial shakedown run with plutonium during which some equipment problems were encountered and corrected, the mixer-settlers were emptied, and the initial plutonium experiment was resumed, as run PX-2. After about 6 h operation and overnight shutdown, the flows were restarted and sampling was begun. Sampling results (Fig. 2.11) showed a decline in uranium concentration from its peak, following an increase in the organic backscrub rate at 215 min. Over the final 90 min of the run, the average plutonium concentration of 4.2 g/liter was in good agreement with the expected value.

Fig. 2.11. Metal concentration in the 1BP product stream vs time, experiment PX-2. Organic backscrub, 1BS, was increased from 0.25 to 0.28 ml/min at 215 min at 42 to 44°C.

The plutonium concentration was in the range of 30 to 37% (of the U+Pu) over the final 400 min of the experiment (Fig. 2.11). Plutonium losses to the two waste streams were less than 0.001% (1AW) and less than 0.0001% (1CW); loss to the uranium strip product stream was about 0.01%. Conditions for the experiment are shown in Table 2.17.

Table 2.17. Experimental conditions for coextraction — partial partitioning run PX-2

Stream	Solution composition	Flow rate, ml/min
1AF	277 g/liter U — 2.92 g/liter Pu — 3 M HNO ₃	0.42
1AS	0.5 M HNO ₃	0.17
1AX	30% TBP—NPH	1.45
1BX	0.06 M HAN—0.1 M N ₂ H ₄ — 0.2 M HNO ₃	0.30
1BS	30% TBP—NPH	0.29
1CX	0.01 M HAN—0.02 M N ₂ H ₄ — 0.01 M HNO ₃	1.9

Results of a second plutonium experiment, in which the 1AS acidity was increased from 0.5 M HNO₃ to 1 M HNO₃, are incomplete. However, the plutonium concentration in the 1BP stream was in the desired range of 25 to 40% of the total heavy metal concentration over the final 400 min of the run. An in-line electrical conductivity cell supplied by J. E. Strain of ORNL Instrumentation and Controls Division provided an excellent measure of acid concentration in the 1BP stream. The resulting calculation of heavy metal concentration from density measurements provided the information needed for composition control.

2.4.6 Solvent Extraction Test Facility

L. J. King, D. E. Benker, J. E. Bigelow, E. W. Brown, E. B. Cagle, F. R. Chattin, E. D. Collins, S. C. McGuire, D. B. Owsley, R. G. Ross, H. C. Savage, R. C. Shipwash, C. E. Waddell, and A. V. Wilder

The Solvent Extraction Test Facility (SETF) in cell 5 of the Transuranium Processing Plant (TRU) is being used for the evaluation and demonstration of solvent extraction flowsheets and flowsheet improvements that are either developed in laboratory studies or identified as potential improvements. The capacity of the solvent extraction equipment for irradiated power reactor fuels is in the kg/d range.

The final solvent extraction run of SETF campaign 2, run 2-SX-4, was completed during July 1979. This two-part run was made to demonstrate the first two cycles of the current HEF flowsheet. The first part was a codecontamination (coextraction-costripping) run. Following batchwise reduction of plutonium and acid adjustment of the uranium-plutonium solution, the uranium was selectively extracted to partially partition the uranium from the plutonium in a second solvent extraction run. A diagram of the flowsheet is shown in Fig. 2.12, and the flow rates and solution compositions are listed in Tables 2.18 and 2.19.

Codecontamination cycle (run 2-SX-4A). The feed solution was formulated to contain approximately 140 g/liter of uranium, 14 g/liter of plutonium, and 4 g/liter of fission product elements. These concentrations are similar to those that would be produced in processing mixed core and blanket fuel from a fast breeder reactor. The feed solution was prepared by dissolving irradiated LWR fuel, containing about 2 kg of uranium, 20 g of plutonium, and 65 g of fission product elements, and adding about 200 g of plutonium that had been recovered in previous SETF operations. The dissolved fuel was from the H. B. Robinson-2 PWR and had been irradiated to 31,364 MWd/t and cooled for five years.

Fig. 2.12. HEF flowsheet used for run 2-SX-4.

Table 2.18. Flow rates and solution compositions for the coextraction-costripping run 2-SX-4A

Stream	Flow rate (liter/h)	Relative flow rate (HAF = 1.0)	Solution composition
HAF	0.785	1.0	3.3 M HNO ₃ —144 g/liter U—13.5 g/liter Pu
HAX	1.52	1.93	30% TBP in NPH ^a
HAS	0.20	0.26	0.8 M HNO ₃
HAIS	0.11	0.14	3.0 M HNO ₃
HCX	1.69	2.15	0.007 M HNO ₃ —0.002 M HAN—0.0005 M N ₂ H ₄
HCIX	0.16	0.20	3.1 M HNO ₃

^aNormal paraffin hydrocarbon diluent.

In the codecontamination cycle, plutonium losses to the HAW and HCW streams were 0.00064% and 0.0018%. The uranium losses were less than 0.0012% in both streams although the uranium stripping was relatively difficult as illustrated by the concentration profiles shown in Fig. 2.13.

Decontamination factors (DF) for the uranium-plutonium product from the first cycle were 2.7×10^5 for ¹⁴⁴Ce, 2.2×10^5 for ¹³⁷Cs, and 3.7×10^3 for ¹⁰⁶Ru. The ruthenium DF obtained in the extraction-scrub bank was 3.4×10^3 . This value is similar to results obtained in previous SETF runs. However, more of the extracted ruthenium stripped along with the uranium and plutonium (the strip bank DF was 1.1) during run 2-SX-4A; in previous runs, only 2 to 20% of the extracted ruthenium was stripped (DF = 4 to 84). This effect is apparently due to the higher stripping temperature (50°C) in run 2-SX-4A compared to either 30 or 40°C in previous runs.

Table 2.19. Flow rates and solution compositions for the selective uranium extraction run 2-SX-4B

Stream	Flow rate (liter/h)	Relative flow rate (1AF = 1.0)	Solution composition
1AF	1.07	1.0	1.2 M HNO ₃ —43 g/liter U—4.5 g/liter Pu
1AX	0.40	0.37	30% TBP in NPH
1AS	0.125	0.12	0.09 M HNO ₃ —0.02 M HAN—0.01 M N ₂ H ₄
1AIS	0.06	0.055	2.9 M HNO ₃
1CX	0.36	0.34	0.01 M HNO ₃

Fig. 2.13. Costripping bank concentration profiles (run 2-SX-4A).

Samples of the waste organic solution (HCW) were taken for laboratory tests. A plutonium retention test indicated that the solvent contained about $2 \times 10^{-5} M$ DBP, which is only seven times that indicated for fresh, carbonate-washed solvent. Samples of the waste organic solution were batch-stripped with equal volumes of Na_2CO_3 or HNO_3 to determine their capability for removing alpha (Pu) and gamma (Ru) emitters. More than 98% of the alpha and 98% of the gamma activities were removed by the carbonate wash at 25°C . About 91% of the gamma and less than 1% of the alpha activities were removed with $6 M \text{HNO}_3$ at 60°C ; only about half of each activity was removed with $0.1 M \text{HNO}_3$ at 60°C .

Selective uranium extraction (runs 2-SX-4B and 2-SX-4C). The uranium-plutonium product solution ($0.36 M \text{HNO}_3$) was divided into three batches each of which was treated by (1) addition of hydroxylamine nitrate (HAN) and hydrazine (mole ratio of $\text{HAN}/\text{N}_2\text{H}_4/\text{Pu}$ was $4/0.27/1$), (2) digestion at 40°C for 2 h, and (3) acidification to approximately $1.3 M \text{HNO}_3$. The amount of Pu(IV) in the three batches after the digestion period was 0.7, 1.3, and 0.8% of the total plutonium and after the acidification was 3.0, 4.1 and 1.9% respectively.

Immediately after acidification, each batch of feed solution (containing about 45 g/liter of U and 4.5 g/liter of Pu) was filtered and then fed to the mixer-settler tank for extraction of part of the uranium. The extraction bank temperature was 26°C during the processing of the first two batches of feed solution (run 2-SX-4B) and was increased to 50°C (run 2-SX-4C) during processing of the third batch. The plutonium concentration profiles, showed a small degree of refluxing while the bank was at 50°C ; however, the plutonium losses (via extraction) at both temperatures were small (0.0037% at 26°C and 0.0052% at 50°C). The degree of uranium extraction during both parts of the run were less than the desired 80% (59% at 26°C and 47% at 50°C), and therefore, the plutonium contents of the U-Pu product solutions were about 17 and 21%, respectively, which is lower than the desired minimum value of 25%.

2.5 Product Conversion

D. J. Crouse

2.5.1 Uranium-thorium and uranium-plutonium coprecipitation with peroxide

J. C. Mailen, D. R. McTaggart, and J. W. Storey

Coprecipitation of uranium-plutonium and uranium-thorium peroxides is being examined as a method for preparing mixed-oxide fuels. Precipitations of U-Th peroxide were completed, and mixed-oxide products have been transferred to the ORNL Metals and Ceramics Division for reduction of the uranium oxide with hydrogen and pellet fabrication. The approximate solubilities of uranium and thorium in acidic peroxide solutions at 15°C are given by the following expressions:

$$K_U = \frac{[\text{UO}_2^{2+}][\text{H}_2\text{O}_2]}{[\text{H}^+]^2} = 1.5 \times 10^{-3} ,$$

$$K_{\text{Th}} = \frac{[\text{Th}^{4+}][\text{H}_2\text{O}_2]^{3/2}}{[\text{H}^+]^4} = 2.8 \times 10^{-3}$$

Thorium was observed to precipitate more slowly than uranium. The first batch of $\text{UO}_3\text{--ThO}_2$ (about 20% Th–80% U) prepared by peroxide precipitation and calcination at 325°C was studied by thermal gravimetric analysis techniques; a peak was observed at 450°C indicating that this material should be calcined at higher than 450°C . The surface area after calcination at 600°C was $8.1\text{ m}^2/\text{g}$. A pellet fired at 1700°C for 6 h had a density of 9.83 g/cm^3 , which is approximately 92% of theoretical density.

2.5.2 Preparation of uranium-plutonium oxide by thermal denitration

C. R. Sherman (Rockwell-Hanford Operations Subcontract)

The Micromeritics surface area equipment within the Analytical Laboratory has been repaired and is now being calibrated. This will provide surface area analyses for both the FY 78 and FY 79 thermal denitration test run materials.

The final reduction runs for conversion of the precalcined mixed-oxide powders (conversion from $\text{UO}_3/\text{U}_3\text{O}_8/\text{PuO}_2$ to UO_2/PuO_2 powders) were completed. The powders are being characterized by the Rockwell-Hanford Analytical Laboratories and by the Hanford Engineering Development Laboratory.

2.6 Analytical Chemistry Development

D. A. Costanzo

2.6.1 Chemical methods development

D. A. Costanzo

Potentiometric titrimetry (C. S. MacDougall). An evaluation is underway of a technique for separating macro quantities of uranium from fission products prior to the Davies-Gray uranium titration. The uranium, in sulfate form, is loaded onto an anion exchange column (Dowex 1A-1X8, 50–100 mesh). Fission products and impurities are eluted by successive washes with $0.01\text{ M H}_2\text{SO}_4$, 10 M HCl , and 6 M HCl , in that order. The uranium is then eluted with about 0.05 M HCl . This uranium eluate is fumed three times with H_2SO_4 , then titrated potentiometrically. Tests gave recoveries of $99.65 \pm 0.08\%$ on uranium standards.

Ion chromatography (J. M. Keller). Ion-pair liquid chromatography (IPLC) employing quaternary alkyl-ammonium salts and conductivity detection is a likely alternative to ion chromatography (IC) for the analysis of DBP and MBP. This technique involves forming the ion-pair of the cationic quaternary alkyl ammonium with the anionic alkyl phosphates. Then under equilibrium conditions, which favor the nonionized state, this complex can be separated on a reverse-phase IC column and then detected conductometrically. This technique should provide several advantages over IC. The needed materials and instrumentation have been received and the IPLC system is being set up to investigate the applicability of this method for the analysis of DBP and MBP.

Other applications of IC have indicated that quantitative separation of divalent cations of Mg, Ca, Sr, and Ba are possible. Also, a new type of anion exchange column for the IC permits the analysis of anionic species which tends to irreversibly bind to the standard columns. Separations have included a mixture of iodide, thiocyanate, and chromate (50 ppm) in the presence of 1 N sulfuric acid. Good separation of the chromate from the predominant sulfate was observed.

2.6.2 Mass spectrometry development

J. A. Carter

Spark-source mass spectrometry development (R. J. Warmack, D. L. Donohue, W. H. Christie, and J. A. Carter). A work order was approved for the fabrication and installation of the high-level gamma spark-source mass spectrometer facility. Major component parts, including master/slave manipulators, shielding window, bellows subassembly, and rail bearings were ordered. Fabrication of the source enclosure was handled by the general machine shop and is essentially complete. Modifications to the mass spectrometer for remote operation are in progress. Completion of the installation is expected before the end of the calendar year.

2.6.3 Nuclear and radiochemical methods development

L. C. Bate and J. R. Stokely

Development has been completed on a neutron activation analysis method for determination of ^{99}Tc in solutions of fission products. A laboratory procedure was written for routine application of the method.

An improved gas train apparatus for analysis of ^{14}C in gas samples and reactor fuel solutions was constructed and tested. The apparatus provides quantitative collection of ^{14}C for liquid scintillation counting and will permit an approximate threefold reduction in the time required for ^{14}C analyses. The new apparatus is presently being installed in the analytical support laboratory in Building 3019.

2.6.4 Instrumental methods development

X-ray fluorescence (XRF) systems development (J. H. Stewart, Jr.). The x-ray fluorescence (XRF) analyzer system for the analysis of nonradioactive materials was installed, tested, and calibrated in the new Building 2026 laboratory. It was then placed in full operational status on August 1, 1979. Construction of the new glovebox-interfaced XRF unit, designed for the analysis of high-alpha/low-beta-gamma materials, was completed and shipped to ORNL.

Capability has been established for the analysis of uranium and zirconium in aqueous and in TBP-dodecane solutions. New XRF procedures have been developed to determine ruthenium in HCl and in TBP solutions and to determine phosphorus in TBP-dodecane (or Amsco). Also, an improved procedure for uranium has reduced the detection limit to less than $1\text{ }\mu\text{g/ml}$ in aqueous solution from $10\text{ }\mu\text{g/ml}$.

Hot-cell analytical instrument development (L. N. Klatt). An instrument for estimating the TBP concentration in hydrocarbon solvents by measuring the dielectric constant of the mixture are completed. Samples containing up to 35% TBP dissolved in any hydrocarbon solvent can be accurately measured. Interference from dibutyl phosphate, monobutyl phosphate, and phosphoric acid are minimized by washing these species from the solvent with dilute aqueous Na_2CO_3 and water.

2.6.5 Laboratory studies

D. A. Costanzo

A study of nitric acid-sugar denitration reactions (C. S. MacDougall). The HEF flow-sheet includes reduction of the HNO_3 concentration of high-level waste by reaction with

sugar prior to waste calcination. The reaction rates of sucrose with concentrated nitric acid in the presence of low levels of iron are being examined more closely. In the first experiment, 50 ml of 2.5 *M* sucrose (0.125 moles) was reacted with 400 ml of 15.7 *M* HNO₃ (6.3 moles) at 100°C. The second experiment was basically the same except that the reaction medium contained 0.1 *M* Fe³⁺. The denitrations were observed for 25-h periods. Several observations were made: (1) There is no observable induction period as had been noted in earlier work with sugar and 7 *M* HNO₃; the reaction appears to begin vigorously as soon as the sugar is introduced in the HNO₃. (2) About 34 moles of HNO₃ are destroyed per mole of sugar reacted. (3) About 25 h of reaction were necessary to eliminate carbon residues. Addition of ferric ion did not appreciably change the efficiency of the reaction or the time necessary to complete the reaction.

2.7 Analytical Chemistry Development (SRL)

J. D. Spencer, M. L. Hyder, and E. J. Lukosius

2.7.1 Evaluation of the LASL x-ray absorption edge densitometer

W. C. Mosley, Jr. and L. W. Reynolds, Jr.

The Savannah River Laboratory has completed the evaluation of an L-x-ray absorption-edge densitometer (XRAED), which was designed and built by Los Alamos Scientific Laboratory (LASL) to accurately assay uranium and plutonium concentrations in process solutions. In earlier reports, an XRAED operation was outlined,¹⁴ an assay of uranium solutions was evaluated,¹⁴ and an assay of uranium-plutonium process solutions indicated a possible effect of the presence of hydroxylamine nitrate (HAN).¹⁵

The effect of the HAN was found to be due to iron impurity, which interfered with the chemical analysis for plutonium. Therefore, a series of mixed uranium-plutonium solutions that did not contain HAN was prepared for evaluation. Also, the plutonium analysis was modified to correct for the effect of the iron impurity in the HAN. A series of 1BP process solutions was assayed, and the results were compared to chemical analysis by the modified procedure. Unfortunately, previous plutonium analyses of process solutions could not be corrected and, therefore, are not useful for densitometer evaluation.

A coulometric method for the accurate analysis of plutonium in BP process solutions was developed to support the XRAED evaluation. Plutonium is quantitatively oxidized on a gold electrode in nitric acid at a controlled potential, which eliminates uranium interference. The relative standard deviation for accuracy in BP process solutions is 0.4%.

The evaluations with mixed uranium-plutonium standard solutions and process solutions have shown that the XRAED can assay uranium above 20 g/liter to within ±0.8% and plutonium at 10 g/liter to ±3% and at 2 g/liter to ±12% respectively.

2.7.2 Thorium determination

E. W. Baumann

To provide a high-precision thorium method that can be used remotely, systems that can use ion-selective electrodes (ISE) for potentiometric titration of thorium are being investigated. A Mettler Instrument Company automatic titrator is being used for this purpose.

A previously published method,¹⁶ which uses EDTA as titrant and a copper SE, has been improved by substituting a cadmium SE. With this electrode, the potential change at

the equivalence point is increased about tenfold. The relative standard deviation is improved from 0.7% in the original method to less than 0.4%, which approaches that of EDTA titrations with visual indicators ($\sim 0.2\%$).

The cadmium SE has a high sensitivity, but the response at the equivalence point is slow. Therefore, other electrodes and other systems are being investigated.

2.7.3 Analysis of TBP degradation products by ion chromatography

J. G. Smith

Work was started to determine the capability of the ion chromatograph (IC) to measure dibutyl phosphate (DBP) and monobutyl phosphate (MBP).

Under standard operating conditions for the IC anion system, DBP elutes almost simultaneously with F^- , and MPB elutes at nearly the same time as phosphate. By increasing the pH sufficiently (with NaOH), phosphate can be caused to elute later as either a divalent or trivalent ion resulting in separation from MBP. The use of 0.001 *M* NaOH–0.002 *M* Na_2CO_3 eluent eliminated the PO_4^{3-} interference; however, DBP and F^- were only partially resolved. The eluent, 0.003 *M* NaOH, was also tested. The DBP and F^- were almost completely resolved; however, MBP was not eluted even after several hours.

2.8 Materials Compatibility

J. C. Griess

The experimental work for this task is carried out under two subcontracts, one with Battelle Columbus Laboratories and the other with Westinghouse Advanced Reactors Division. Progress during the quarter is summarized below.

2.8.1 Corrosion studies at Battelle Columbus Laboratories

J. A. Beavers, W. K. Boyd, and W. E. Berry

Iodox process system. Corrosion associated with hot concentrated magnesium nitrate solutions used in the production of very concentrated HNO_3 was assessed. Titanium and types 304L and 316L stainless steel experienced negligible corrosion in boiling solutions containing up to 70% $Mg(NO_3)_2$. However, with the addition of 1% HNO_3 to the $Mg(NO_3)_2$ solutions, both stainless steels corroded at rates up to 265 $\mu m/year$ (11 mpy); titanium was unaffected. None of the three materials showed any tendency to undergo stress corrosion cracking. In view of these results, titanium is the preferred material for the Iodox equipment that handles concentrated magnesium nitrate solutions.

Off-gas system. An evaluation of the effect of the water content of air-containing iodine on corrosion of several materials was completed. The results showed an increasing attack on stainless steels with increasing water content. At very low water concentrations, only a dark solid formed on these materials; however, within 5 min after being removed from the test container and exposure to laboratory air, the deposit changed to a dark liquid under which pits formed. With higher water contents in the gas stream, a corrosive liquid formed directly. Titanium, zirconium, Hastelloy C-276 and Inconel 625 remained free of attack under all conditions. Tests were recently begun to evaluate the effect of iodine concentration and of NO_2 in the iodine-water-air mixture on the corrosion of several materials.

Tests in 5.5 M hydriodic acid (HI). Tests of 500-h duration were completed in boiling 5.5 M HI with welded specimens of zirconium, Hastelloy C-276, Hastelloy G, and Inconel 625. Leaching of plutonium from primary dissolver residues with HI is being considered as an alternative to leaching with HNO_3 -HF. Since previous data had shown that the presence of air accelerated attack on the latter three alloys, attempts were made to keep air from entering the test containers, but judging from the variable incremental corrosion rates, attempts were not totally successful. Exclusion of at least gross amounts of oxygen would be necessary in practice to prevent oxidation of HI. The corrosion rates averaged over the 500-h period were less than 2.5, 38, 150, and 765 $\mu\text{m}/\text{year}$ (<0.1 , 1.5, 6, and 30 mpy) for zirconium, Hastelloy C-276, Inconel 625, and Hastelloy G respectively. Neither the weld metal nor the heat-affected zones of welds showed preferential attack.

2.8.2 Corrosion studies at Westinghouse Advanced Reactors Division

P. C. S. Wu, C. R. Simmons, and N. L. Haines

Corrosion tests at Westinghouse are limited to acid fluoride solutions typical of those used for dissolution of thorium-containing fuels and for dissolving plutonium from residues remaining after treatment of plutonium-uranium fuels with nitric acid.

Tests with type 304L stainless steel and Inconel 671 in boiling 13 M HNO_3 –0.05 M HF solutions to which various complexing agents (Al, Zr, Th, fission products) were added produced confusing results. In nearly all cases, corrosion rates increased with time, and the rates were much higher than observed on the same materials during screening tests in similar solutions. Furthermore, attack on Inconel 671 was as high, and sometimes higher, than on type 304L stainless steel, which is contrary to the results from the screening tests.

Although the reasons for these results are not completely clear, two factors are probably responsible for at least a large part of these observations. First, Cr(VI), a corrosion accelerator, formed in these solutions, but the rate at which it formed was not determined. Secondly, in the present tests, the Inconel 671 test specimens were made from 6.4-mm-thick plate, whereas 3.2-mm-thick sheet was used in the screening tests. It is possible that with the thicker plate, the quenching rate after annealing, was not rapid enough to prevent the segregation of alpha chromium accompanied by the formation of a nickel-rich phase. This latter phase would likely be highly susceptible to attack in HNO_3 -HF solutions, particularly in the presence of Cr(VI).

References

1. W. D. Burch et al., *Advanced Fuel Recycle Program Progress Report for Period January 1 to March 31, 1978*, ORNL/TM-6303 (May 1978), p. 2-18.
2. A. S. Gorden, "The Reaction Between Hydrazine and Hydrogen Peroxide in the Liquid Phase," p. 493 in *Proc. Third Symp. Combustion and Flame Explosium Phenomena*, Williams and Wilkins, Baltimore, Md., 1949.
3. A. D. Kelmers, L. Maya, D. Y. Valentine, and W. Davis, Jr., *Kinetics of the Hydroxylamine-Nitrous Acid Reaction in Nitric Acid Media*, in preparation.
4. M. N. Hughes and G. Stedman, *J. Chem. Soc.* 2824 (1963); T. D. B. Morgan, G. Stedman, and M. N. Hughes, *J. Chem. Soc. (B)*, 344 (1968).
5. W. D. Burch et al., *Consolidated Fuel Reprocessing Program Progress Report for Period April 1 to June 30, 1979*, ORNL/TM-6994 (September 1979), p. 2-13.
6. Ref. 5, p. 2-15.

7. *Savannah River Laboratory Technical Progress Report, Consolidated Fuel Reprocessing Program, October 1978–March 1979*, USDOE Report DP-CFRP-79-1-1, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S.C. (1979), p. 1-25.

8. *Savannah River Laboratory Quarterly Report, Alternate Fuel Cycle Technologies, April–June 1977*, USERDA Report DPST-AFCT-77-1-2, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S.C. (1977), p. 39.

9. *Savannah River Laboratory Technical Progress Report, Consolidated Fuel Reprocessing Program, April–June 1979*, DP-CFRP-79-1-2, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S.C. (1979), p. 4-1.

10. W. D. Burch et al., *Consolidated Fuel Reprocessing Program Progress Report for Period January 1 to March 31, 1979*, ORNL/TM-6836 (June 1979), p. 2-56.

11. S. B. Watson and R. H. Rainey, *Modeling the Effect of Temperature on Thorium and Nitric Acid Extraction and the Formation of Third Phase for Modification of the SEPHIS-Thorex Computer Program*, ORNL/CSD/TM-69 (May 1979).

12. A. J. Weinberger, J. L. Marley, and D. A. Costanzo, *A Solvent Extraction Study of the Thorium Nitrate, Nitric Acid, Tributyl Phosphate/Dodecane System*, ORNL/TM-6875 (in preparation).

13. Ref. 10, p. 6-12.

14. Ref. 7, p. 6-1.

15. Ref. 9, p. 6-1.

16. E. W. Baumann and R. M. Wallace, *Anal. Chem.* **41**, 202 (1969).

3. ENGINEERING RESEARCH

W. S. Groenier

The various engineering research studies summarized here represent the first phase of the equipment development program and provide a basis for further design and development of specific engineering test components. Emphasis is placed on the identification, study, selection, development, and characterization of unit processes through the application of basic or fundamental experimental engineering techniques.

Studies of the voloxidation, dissolution, feed preparation, solvent extraction, and off-gas treatment processes are in progress, and development efforts are described. Work directed toward dissolver and solvent extraction equipment development is also reported.

Most ongoing activities are reported in summary fashion, with the intent being to place details in topical reports. By way of introduction, work that is new to this section is described in greater detail than ongoing work.

3.1 Voloxidation

M. E. Whatley

The voloxidation process is being developed as a head-end method for removing tritium from spent uranium reactor fuel prior to aqueous processing. Based on experimental work, it appears that this objective can be met by reacting the oxide fuel with oxygen or air in a temperature range of 450 to 650°C (723 to 923 K). The release of tritium and, to a lesser extent, some of the other fission products occurs when UO_2 is restructured to U_3O_8 during oxidation. The early removal of tritium from the fuel into a relatively small volume is desirable to avoid mixing the tritium as water with aqueous streams in subsequent process steps. A secondary benefit of voloxidation is the oxidation of residual sodium in the fuel prior to dissolution.

An investigation of the applicability of rotary kilns to the voloxidation process has been continued by (1) performing heat transfer tests using a small rotary kiln, (2) initiating a kiln-seal evaluation study, and (3) continuing an erosion-corrosion test to evaluate candidate materials of construction. Tests of a 0.5-t/d voloxidizer system are described; this effort represents the major portion of our involvement this year. The continuing evaluation of molecular sieves for tritium retention is also described.

3.1.1 Component development

T. D. Welch, B. B. Spencer, and M. E. Whatley

An experimental voloxidation system scaled to 0.5 t/d has been provided to study (in nonradioactive experiments) certain important process parameters and the applicability of some full-scale standard commercial equipment components, to extend and verify basic data on heat and mass transport in the voloxidation system, and to address the problems of process control.

Work this quarter addressed the problem of solids spilling into the inlet breaching section and the operation of the off-gas filter. Improvements were also made in the Bristol hardware and software.

The flights being developed for the inlet section of the kiln performed adequately under conditions simulating normal operation. However, experiments at 15% solids loading showed unacceptable solids spill for all inlet concepts tested. Further work is in progress to solve this problem. We anticipate that replacement flights can be installed in the full-scale experimental voloxidizer (FSEV) next quarter. A system for pneumatic conveying of the spillover solids was installed and will be tested next quarter.

A commercial filter cartridge was installed in the off-gas line and operated satisfactorily during several tests. The gas face velocity was maintained below 6 ft/min for these tests.

Changes were made in the Bristol unit process controller to improve control and data transmission and to aid operation.

The 1-t hoist and color CRT will be installed in September. No delivery dates are available for the telemetry system or the replacement drum.

3.1.2 Rotary-kiln heat transfer studies

B. B. Spencer and M. E. Whatley

Twenty-five experiments have been performed to measure the gas-phase heat-transfer characteristics using the equipment described previously.¹ In these runs, the rotational speed was varied from 1.2 to 7.5 rpm, the temperature was 300 or 400°C, and the air flow rate varied from 0 to 1.486 scfm. The differential equation that describes the gas-phase temperature profile is, at steady state,²

$$\mathcal{D} \frac{d^2 T}{dX^2} - V \frac{dT}{dX} + \frac{\pi D h}{A \rho C_p} (T_w(x) - T) = 0, \quad (3.1)$$

where

- A = cross-sectional area available for gas flow in kiln,
- C_p = heat capacity of gas,
- D = inside diameter of kiln,
- $\mathcal{D}$ = dispersion coefficient of gas phase,
- h = heat-transfer coefficient between kiln wall and gas phase,
- T = temperature of gas phase,
- $T_w(x)$ = temperature of kiln wall as a function of length,
- V = velocity of gas phase through kiln,
- x = kiln length,
- ρ = density of gas phase.

This equation can be solved to yield

$$T = \frac{-\beta}{\mathcal{D}\gamma} \int_0^x T_w(u) e^{\psi(x-u)} \sinh \gamma(x-u) du + \frac{T' - T_0 \psi}{\gamma} e^{\psi x} \sinh \gamma x + T_0 e^{\psi x} \cosh \gamma x, \quad (3.2)$$

where

$$\beta = \frac{\pi D h}{A \rho C_p}$$

$$\psi = \frac{V}{2 \mathcal{D}}$$

$$\gamma = \sqrt{\frac{\beta}{\mathcal{D}} + \psi^2}$$

$$T_0 = T(0)$$

$$T' = T'(0)$$

and u is a dummy variable of integration. The integral expression in Eq. (3.2) can be solved analytically when the kiln wall temperature is described by a polynomial in x (or u). For any given experiment, values for T_0 are given by the measured gas temperature at the kiln entrance. With the measured gas temperature at the kiln exit end, Eq. (3.2) can then be used to calculate a value for T' . Now, with the exception of $\mathcal{D}$ and h , all other parameters are known or can be measured.

A computer code has been written which utilizes the above information and varies the values of $\mathcal{D}$ and h until a best fit of Eq. (3.2) to the remaining data pairs (T vs x) is obtained. This code is currently being tested using the data and is being checked to determine its sensitivity to the types of polynomial used to describe the kiln wall temperature. Additional experimentation is underway.

3.1.3 Tritium retention from voloxidizer process off-gas

W. D. Holland

This activity is being performed under subcontract at Tennessee Technological University to determine the effect of iodine on the operation of a water vapor removal system for the treatment of voloxidizer off-gases. A 2-in.-diam by 30-in.-long bed of molecular sieve pellets is being used to remove water vapor from an air stream containing iodine. A series of experiments is being conducted at gas flow rates and iodine and water vapor concentrations designed to match the expected values of these parameters in a voloxidizer off-gas drying system.

Earlier this quarter, the test column was recharged with new 1/16-in. pellets of Linde type 3A molecular sieves to study the effects of various parameters on regeneration. The initial runs indicated that this bed retained about 15 times more iodine than a similar bed tested last year. Contact with a Linde Division representative revealed that the clay binder

used in the pelletized sieves had been changed to one having a different pore-size distribution. A check of the lot numbers showed that the original sieves were of the older type (type R) whereas the sieves in the newly charged bed had the new type binder (type EPG).

A series of runs was conducted using columns packed with the new material (type 3A-EPG) and the older material (type 3A-R) to explore the differences in iodine and water retention caused by the binder material. The water loading at breakthrough was found to be about 19% for type 3A-EPG and was relatively constant over the period of study, whereas type 3A-R showed an initial loading capacity of about 17%; this value, however, decreased to about 14.5% over the test period. Iodine loading was found to be about 5 g/kg of bed for type 3A-EPG and slightly over 1 g/kg for the type 3A-R material. This latter result is somewhat higher than the 0.4 g/kg of bed found last year for a bed of similar type 3A-R material with a different lot number.

3.1.4 Seals development

J. G. Morgan

Among the most important mechanical features of the rotary-kiln voloxidizer design are the mechanical rotating seals that isolate the kiln atmosphere from the cell atmosphere. Under normal operating conditions, each seal (one at each end of the rotating tube) should leak less than 0.5 cfm into the system when the internal vacuum is about 2 in. H₂O. Firm design criteria have not yet been established for the seals, since any inleakage is detrimental from the point of view of the process. Further, the degree to which the leakage is limited will depend on the results of conceptual design studies.

Installation of the test stand for a prototype reference seal was completed. A full-size rotating seal will be tested under simulated operating conditions. The seal consists of a stationary graphite ring bearing against a rotating flange and bolted to a mockup of the rotary kiln end pipe. Provisions are made to measure seal leakage as a function of differential pressure across the seal and for various amounts of seal misalignment. The seal is designed to accommodate a 5-degree axial, ± 0.5 -in. radial, and ± 1 -in. longitudinal misalignment. It will operate at a temperature of 200°F and rotate at 6 rpm under a 5% relative humidity atmosphere. These accelerated tests allow a six-month life test to be approximated in about 4 weeks.

3.1.5 Rotary-kiln corrosion test

W. D. Holland and M. E. Whatley

Two identical drums (18-in.-diam x 20-in.-long) fabricated from type 316 stainless steel and Incoloy 800H are being used to evaluate these materials for rotary-kiln service.

The drums were loaded with 10 kg each of 1/4-in. type 304L stainless steel rods sheared to 1-in. lengths. As reported previously, no measurable thickness change was found in the test sections of either material after 75 d rotation at 1 rpm and a temperature of 650°C. The test is continuing with a new 10-kg charge of stainless steel rod along with 1 kg of sand; the results will be provided when available.

3.2 Dissolution

J. Q. Kirkman

The objective of the dissolution task is to ensure that LMFBR fuels can be dissolved in nitric acid to give high metal recoveries. Criticality control and off-gas considerations require dissolver design and operation to be performed within rather narrow limits. Continuous dissolving methods, which appear to offer superior solutions to these and other problems, are being emphasized.

During this reporting period, emphasis has been placed on the ongoing development of a continuous rotary dissolver. In addition, work has continued on an advanced dissolver design concept and on the development of a method for providing solids agitation in a digester tank.

3.2.1 Rotary dissolver erosion-corrosion tests

B. E. Lewis

Continuation of the dissolver erosion-corrosion tests has again been delayed by bearing problems. During the checkout period following the installation of the Graphitar-114 bearings, several motor stallouts occurred. These were later attributed to the buildup of powdered Graphitar bearing material between the support roller shaft and bearing sleeve resulting in seizure of the shaft by the support roller. Problems similar to these were experienced previously with the prototype dissolver. Stainless-steel ball bearings have been purchased to replace the damaged Graphitar bearings. One of the new bearings has been successfully tested submerged in 8 M HNO_3 for approximately 228 h. No signs of structural deterioration were noted; a net weight loss of about 10 g was attributed to the removal of the bearing packing grease by the nitric acid. The discoloration of the bearing surface can probably be accounted for from the deterioration of the packing grease.

The front support bearings of the dissolver have been replaced. The rear bearings are ready to be installed as soon as the two thrust bearings are replaced. This work should be completed by October.

Some difficulty has been experienced with the HNO_3 concentration control loop. One problem was a blocked control valve in the acid feed line to the make-up tank. It has been repaired and tests are underway to measure the operating efficiency of the Dynatrol unit.

3.2.2 Advanced rotary dissolver development

B. E. Lewis

Various modifications have been made to the advanced rotary dissolver model including an enlargement of the support platform to accommodate a small vibratory solids feeder and the installation of a variable-speed drive motor so that dissolver operation may be studied at various rotational rates.

The search for a small-scale simulated fuel material has indicated that it may be necessary to sacrifice some on the size of the fuel because of problems with adherence of the simulated fuel to the walls of the dissolver.

A test program is being prepared that will satisfy the overall goals of the project and provide input for the design of a larger scale dissolver.

3.2.3 Digester study

B. E. Lewis

The basic fabrication of the Plexiglas digester tank and test stand is complete. The system is currently being installed in the basement of Building 7603. Various pieces of support equipment are being designed and fabricated while a light detection system for the determination of the degree of solids suspension is provided. Photocells and infrared light-emitting diodes (LED's) will be used to monitor the solids concentration profile in the digester tank. The infrared light region was chosen to eliminate the effects of variable ambient light on the concentration readings.

3.2.4 Flow modeling studies

B. E. Lewis

Debugging the dissolver stagewise material balance program, MATL. BAL, is continuing. Some very crude experiments have been conducted to get an order-of-magnitude type estimate of the amount of fuel released from the fuel pins during tumbling and falling in the rotary dissolver. Porcelain-filled hulls (1/4-in.-diam x 1-in.-long) were used to simulate the sheared fuel pins. The experiments consisted of dropping the simulated fuel pins through approximately 2 ft of air and 2 in. of water onto a stainless steel pan. The release rate of fuel from the fuel pins is required by the MATL. BAL program in determining the quantity of fines suspended in the dissolver solution.

A second computer code has been under development to predict the outlet concentration and flow from the pilot plant dissolver when subjected to a step change in feed flow and acid concentration. Initially, an idealized step-change response based on the mixed-tanks-in-series model was used. Data from experiments conducted with the prototype dissolver were compared with the model predictions. It was found that the model predicted the output response too soon. The mixed-tanks-in-series model assumes a constant flow to and from all stages; however, this is not the case in the prototype dissolver. It was found that the flow between dissolver stages at zero rpm can be approximated by a modified weir equation, and when used in conjunction with a stagewise differential mass balance, yields a much more satisfactory model. However, increasing the rotational rate also has an effect on the step-change response. Generally, it appears to increase the stage holdup and, therefore, lengthens the time required to reach steady-state. Experiments are being run using the prototype dissolver in an attempt to quantify this effect. The results from the rotational rate experiments will be combined with the zero rpm findings to get a more widely applicable prediction of the dissolver flow characteristics.

3.3 Feed Preparation

W. S. Groenier

The aqueous feed discharged from the primary dissolver system will contain solids (undissolved fission products, corrosion products, etc.) and, therefore, will require clarification prior to solvent extraction. Preparation of the feed for solvent extraction will also include adjustment of the plutonium valence and the nitric acid concentration, as well as treatment to remove iodine. This task also encompasses the development of secondary dissolution methods (with more corrosive reagents and for fuel constituents not soluble in the primary dissolver), accountability systems, and fluid transfer and metering systems.

Since the large amount of nitrogen oxides in dissolver off-gas streams has a deleterious effect on the performance of the Iodex process for removing iodine from gas streams, the development of a method to remove these contaminants has also received considerable attention.

3.3.1 Iodine evolution tests

J. G. Morgan

A topical report is being prepared to summarize all of the iodine evolution work, including both static and continuous methods. The "Highlights" of this report state that:

Two methods are considered for the removal of radioiodine from fuel reprocessing acid streams: (1) continuous steam stripping and (2) air sparging in the digester tanks. Bench-scale experiments were conducted to examine both methods using ^{131}I as a tracer in 4 M HNO_3 . The steam-stripping method used a continuous flow, which was equivalent to that projected for a plant designed to process fuel at the rate of 0.5 t/d. This flow entered the top of a packed distillation column; more than 97% of the iodine was removed. Iodine removal efficiency was determined as a function of column height, inlet flow rate, and boiling rate. The amount of nonvolatile iodine remaining in the bottoms stream could be reduced by adding hydrogen peroxide to the boiler.

Iodine removal from a 4 M HNO_3 solution was also studied using an air sparge in a small tank. Mass transfer coefficients were measured as a function of temperature, air sparge rate, and iodine concentration, and were used in an example of a design for a full-scale digester tank.

3.3.2 Nitrogen oxide scrubbing tests

R. M. Counce

Engineering activities to study the removal of nitrogen oxides from gaseous mixtures of NO_x , N_2 , and O_2 in packed scrubber towers have continued. During this report period, efforts have centered on continuing the development of a mechanistically based numerical simulation of NO_x absorption in packed scrubber towers. This simulation incorporates mathematical models for the various absorption/desorption mechanisms that appear to contribute to the scrubbing of the gaseous NO_x species. The development of the overall simulation and its supporting models is proceeding by adjusting the relative importance of the various mechanisms until the simulation produces results that agree reasonably well with experimental data. The culmination of these activities will result in a computer program that will simulate NO_x absorption in packed towers for process control and design purposes.

3.3.3 Fluid transfer and metering

R. M. Counce

Engineering studies have been initiated to investigate the feasibility of fluid transfer by fluidic pumping. The preliminary experiments described here give some insight into this developmental pumping concept.

A flow diagram of the fluidic pump test facility is shown in Fig. 3.1. The major components are the feed and receiver tanks, a pumping chamber, a venturi diode, valves and piping to simulate various pumping heads, and instrumentation to measure the system pumping capacity as well as the venturi characteristics. This system has been described in greater detail in a previous report.¹ Pumping is accomplished by the cyclic pressurizing and venting of the pumping chamber. During the vent portion of the pumping cycle, the

process fluid (water) flows under the influence of gravity from the feed tank through the fluid diode into the pumping chamber. When the pumping chamber is sufficiently full, a solenoid valve closes the vent and allows process air to pressurize the pumping chamber. The process solution is forced from the pumping chamber through the double-nozzle diode to the receiver tank. A pressure reduction occurs in the throat of the diode sufficient to prevent the liquid from returning to the feed tank. The pumping chamber is vented when empty, thus beginning a new cycle. The feed tank is refilled when empty by allowing the receiver tank to drain into the feed tank through an appropriate valve.

The following results are from a series of experiments where the motivating pressure was varied from 9.6 to 14.7 psig. The fluid was pumped to a height of about 18 ft above the outlet of the pumping chamber. The total pumping cycle time is the sum of the time required to fill and discharge the pumping chamber. Figure 3.2 shows total and component pumping times as a function of the motivating pressure. Increasing the motivating pressure does not affect the fill time, since the pumping chamber is vented to the atmosphere during this operation; however, it does decrease the time required to force the fluid from the pumping chamber. The decrease in total cycle time with increased motivating pressure is primarily the result of the decrease in the time required for the pumping (or discharge) portion of the pumping cycle.

The flow rate, q , from the pumping chamber increases in response to the motivating (or pumping) pressure. A graph of flow rates during the pumping portion of the overall cycle is shown in Fig. 3.3. The positive flow on this graph is from the pumping chamber into

Fig. 3.2. Total and component pumping times as a function of moving pressure, P_{PC} .

Fig. 3.3. Component flow rates during the pressure portion of the pumping cycle.

the feed and/or receiver tanks. At the lower pumping rates in this experimental series, a fraction of the flow leaving the pumping chamber returns to the feed tank. As the motivating pressure is increased, this fraction decreases and becomes negative, corresponding to the fluid being pumped from the feed tank.

An extrapolation of this data indicates that for motivating pressures less than the required pumping head and greater than the feed tank head, the total flow is back to the feed tank. Thus, this system could be used to agitate the contents of the feed tank in a non-pumping mode of operation.

The total system pumping capacity for the described conditions is presented for various motivating pressures in Fig. 3.4. The regular increase in flow rate with pressure suggests that a convenient flow control system for this type of pump could involve regulation of the motivating pressure. Operations to date under maximum conditions produced flow rates greater than 4 gpm at pumping heads of 42 ft using a motivating pressure of 28 psig.

Fig. 3.4. System pumping rates vs motivating pressure.

This activity will be continued and is scheduled to culminate in a pump design for a specific IET application. A greater understanding of the advantages and disadvantages of fluidic pumping will undoubtedly occur as we obtain more experience and factor in fluidic technology obtained from the British through the USDOE/UKAEA Exchange Agreement.

3.4 Solvent Extraction

M. E. Whatley

The development of solvent extraction techniques for the Purex process recovery of advanced fuels is continuing at Argonne National Laboratory (ANL). The primary objective of the program is to design, fabricate, and test an annular centrifugal contactor of critically safe dimension to reprocess advanced fuels at a rate of approximately 0.5 t/d. The program also includes a supporting laboratory effort.

At ORNL, efforts are underway to improve and apply the SEPHIS computer code for flowsheet engineering studies and to evaluate a mixed-cell contactor for solvent washing.

Additional work is in progress at the General Atomic Company (GA) to evaluate the Robatel solvent extraction contactor and to perform pulsed-column improvement studies.

3.4.1 Centrifugal contactor development

G. J. Bernstein, R. A. Leonard, R. H. Pelton, and A. A. Ziegler (ANL)

Work is continuing on the program to develop improved solvent extraction techniques for the reprocessing of fast breeder reactor fuels. During this quarter, fabrication of the second (12-cm) annular centrifugal contactor sized to process 0.5 t/d of fast breeder reactor

fuel was started and is almost complete. Models and correlations developed using the first (9-cm) contactor were tested further and extended by incorporating data from a 25-cm contactor now being developed for the Savannah River Laboratory. Design has begun on a smaller (4-cm) contactor, a size that should be suitable for the study of the effect of third-phase formation (as can occur in a Thorex process) on contactor operation.

M-2 contactor (12-cm). Fabrication of the 12-cm annular centrifugal contactor (designated M-2) was started this quarter. Construction of the rotor and the housing is essentially complete. Some work remains to be done on the mounting frame. Delivery of the 1-hp motorized spindle by the vendor has been delayed due to a strike at a motor supplier's plant.

In preparation for the hydraulic performance tests, the dispersion-band model was used to calculate the expected contactor performance.

Model development. Models and correlations developed with the 9-cm contactor were tested further and extended using data from the performance of the 25-cm contactor. The dispersion-band model (used to predict hydraulic performance) and the mixing-power model worked well for the larger unit. The degree of mixing in the annular (Couette) mixing zone, as characterized by the dimensionless dispersion number, is essentially unchanged from the 9-cm performance. Further work with the dispersion band model showed that an optional organic weir radius can be calculated. On this basis, the 12-cm contactor will be within 94% of the optimum throughput.

With the addition of the 25-cm performance results, the correlation of liquid height in the Couette mixing zone was extended to include the effect of the rotor diameter. The circular weir correlation was extended to include this larger diameter. Finally, the results of the 25-cm tests indicate a need to develop a model that predicts the critical speed of larger contactor rotors.

Third-phase performance tests. Concern for third-phase formation during Thorex process operations continues to exist. Previous tests on the 9-cm contactor using a third phase of fine polymer powder (with a density between that of the organic and aqueous process phases) suggests that a third organic phase should not create an operational problem. However, there is some evidence, based upon pulsed-column operation, that a third phase (second organic phase) having a higher density than the aqueous phase can develop. If this were to occur "instantaneously," it could interfere with the operation of a bank of centrifugal contactor stages. A 4-cm contactor is being designed as a basis for a multistage contactor that could be used to test actual third-phase formation in a Thorex process and its effect upon contactor operation.

3.4.2 Flowsheet engineering studies

R. T. Jubin and M. E. Whatley

The computer program (MATEX) to predict steady-state concentrations for multistage Pu(IV)-U(VI) solvent extraction systems using matrix techniques was further developed and tested. This code generally converges more rapidly than does SEPHIS and allows for the use of a tighter tolerance. In a comparison test, the computational times required to meet a tolerance of 0.01% change between iterations on a 24-stage system featuring plutonium reflux were 0.55 s for MATEX and 37.37 s for SEPHIS. MATEX yielded a somewhat better material balance, accounting for 99.98% of the material fed. To reach tighter tolerance limits of 0.001% and 0.0001%, MATEX required 0.82 and 0.94 s respectively.

Modifications were also completed to enable MATEX to simulate a multicolumn system. This will allow the user to transfer all or a portion of any stream to any stage in the system. In essence, this is the same as having up to 100 individual ideal equilibrium stages that can be coupled together in any configuration. Another modification allows uranium, plutonium, and nitric acid concentration profiles to be plotted for both phases on a single graph.

The MATEX computer code was used to examine five of the 200-series HEF stripping columns. These were the HC, 1C, 2E, 2B, and 3B columns. Only the 2E column appears to perform as desired with the specified conditions. The other columns require some slight modification in one or more of the following: (1) an increase in the number of stages, (2) an increase in the aqueous flow rate, (3) an increase in the operating temperature, or (4) a change of the IX feed location.

Future plans for the MATEX code include the addition of a plotting package to plot the data representing the operating and equilibrium lines. This will aid in the evaluation of the effect of slight changes in the equilibrium curve and will be used during the evaluation of other HEF columns.

Studies are now in progress to develop a set of conditions that will yield a 5 to 25% plutonium aqueous product stream, with less than 0.1% plutonium loss from a 1% plutonium organic feed stream using no reductant. This feed stream is representative of one found in an LWR reprocessing flowsheet. The most attractive approach to this separation is to use a cascade of ample stages with a large reflux of solutes. Early studies with MATEX have revealed an instability in the convergence of the program under these conditions. Since many future studies are anticipated in this interesting mode of operation, methods for improving the convergence algorithm of MATEX are being investigated. The use of SEPHIS is possible but not attractive since it converges very slowly under these conditions.

The draft of a report presenting the correction terms for Richardson's model of the uranium, plutonium, and nitric acid distribution coefficients has been completed. This correction term was developed using a statistical analysis of the plutonium distribution coefficients. This indicated that a better fit, considering 703 data points (with the following parameter ranges: 0 to 352 g/liter U, 0 to 112 g/liter Pu, 0 to 10 M HNO₃, 30% tributyl phosphate, and temperatures of 0 to 72°C), would be to correct the UCØR values as follows:

$$\text{DPU}_{\text{new}} = \text{DPU}_{\text{old}} / (0.56778 + 0.013118T + 0.74358[U] - 0.17583[U][\text{HNO}_3]) \quad (3.3)$$

where T is in °C, and $[\text{HNO}_3]$ and $[U]$ are in moles per liter on a solute-free basis. The report also contains tabular listings of the distribution coefficients and a program listing and user's guide to DISCOE, the code that generates the distribution coefficient tables and plots.

3.4.3 Solvent washing contactor

W. E. Eldridge

Early studies have shown that the performance of the mixed-cell contactor might be improved by implementing major design changes. The present contactor provides considerably more intense mixing than is considered necessary, and streaming along the wall that bypasses the baffles has been noted. A redesign of the contactor to provide a unit that is better suited to a study of operating parameter values that will substantially improve degradation product removal is being considered.

Sample values (from Analytical Chemistry Division) of gas and ion chromatographic analyses for monobutyl and dibutyl phosphate (MBP and DBP) continue to produce material balances that are highly inconsistent. Further consultations are being held to determine if the capability exists to accurately measure the minute quantities of degradation products present in our system.

Phenolphthalein has been used to establish clarity of the aqueous-organic interface in the phase separation. This practice will be discontinued because of an undesirable reaction between phenolphthalein and the chromatography beds, resulting in a faster degradation of the bed material.

Upcoming work will mainly entail some equipment modification and a follow-up of parametric studies.

3.4.4 Robatel contactor evaluation study

R. D. Zimmerman, G. E. Benedict, and D. R. Engler (General Atomic Company)

At present, the Robatel centrifugal contactor is the only commercially available short-residence contactor suitable for solvent extraction processing of irradiated nuclear materials. Using the Robatel centrifugal contactor installed in the General Atomic pilot plant, experimental testing was completed to determine the suitability of this contactor for uranium extraction and for scrubbing of ^{95}Zr fission products.

In the extraction mode, an LWR flowsheet was used with solvent throughputs of 500-, 1000-, and 1500-ml/min. Corresponding organic residence times are 3.2, 1.6, and 1.1 min, respectively (for the eight-stage contactor). Nine, fourteen, and eight replicates were made at each flow rate while other variables were investigated in a 22-ft cylindrical pulsed scrub column.

After reaching steady-state conditions, all flow rates, both outlet stream temperatures, the rpm, and the motor current were recorded. In addition, the feed and effluent streams for the entire system were sampled for accountability and for efficiency determination. Profile samples were also obtained for the scrub column and for the stripping column. Data analysis is pending.

In the scrub mode, a similar program was carried out. About 200 h operating experience was gained from both programs together.

Trace quantities of ^{95}Zr were added to the feed in five extraction and in three scrub mode runs. A direct comparison of the eight-stage Robatel contactor with a 22-ft pulsed column can be made when data reduction is complete.

A strip-chart recording of the motor current was found to be a suitable indicator of maloperation. Change in rpm, variations in feed flow rate, and flooding are easily identified.

Tests with solids in the feed will be made before the end of the fiscal year. It is anticipated that the machine will plug rapidly under such conditions where an organic-continuous pulsed column continues to operate.

Method development: uranium analysis by ^{238}U -irradiated to ^{239}Np [S. A. Dunlap (General Atomic)]. Low-level uranium analysis is presently being done colorimetrically. Because of lengthy turnover times, a more cost-effective method is being studied. Uranium-238 is irradiated in the General Atomic TRIGA reactor and converted to ^{239}Np , which has a half-life of 2.3 d. The gamma activity of the ^{239}Np is then determined by gamma spectroscopy using a Ge-Li detector. Employing these techniques, the concentration of ^{239}Np and of uranium in standards and samples can be measured in a much shorter turnover time. Present solvent extraction runs include zirconium. These studies have also incorporated zirconium in the irradiation runs.

Initial standards studied contained only uranium. In the range of 10^{-1} to 10^{-5} g/liter, the sensitivity level was found to be 2×10^{-4} g/liter of uranium.

The next studies involved the addition of zirconium to the uranium samples. No interference was observed for uranium in the range of 10^0 to 10^{-5} g/liter in the presence of zirconium at 10^{-1} to 10^{-2} g/liter of zirconium (Fig. 3.5).

Fig. 3.5. Irradiated U-238. (Courtesy of General Atomic)

3.5 Off-Gas Processing

W. S. Groenier

This task consists of the development of various processes for the treatment of re-processing plant off-gases to ensure that environmental goals are met. Work includes the development of the noble gas and ^{14}C selective absorption process (an activity concerned with the expansion of pilot plant development), the formulation of plant engineering design criteria, a study of the chemical effects of impurities in the fluorocarbon solvent, and an extended investigation of the distribution coefficients of the noble gases in the fluorocarbon solvent.

This task also includes the development of the Iodox process for the removal of iodine from off-gas streams. Iodine retention factors approaching 10^7 are desired when processing

90-d-decayed fuel. The Iodex demonstration system incorporates iodine scrubbing with hyperazeotropic nitric acid, the collection of solid pentavalent iodine, and acid recovery. Studies of the Iodex process have been completed.

The use of solid sorbents for various off-gas purification applications will be evaluated as part of the overall effort. The development of a ^{14}C fixation process using barium or calcium hydroxide hydrate is also underway.

Work on an integrated HTGR off-gas treatment system is proceeding at General Atomic Company. Since this system makes extensive use of solid sorbents, it is being reported in this section.

3.5.1 Fluorocarbon absorption process development

M. J. Stephenson, B. E. Kanak, and D. K. Little (ORGDP)

Analysis of the pilot plant data taken from the spring campaign is continuing. The internal condensation zone and resulting noble gas product buildup must be precisely located in the combination column at a vertically-fixed take-off point, otherwise the optimum product concentration cannot be collected. The solvent flow rate largely establishes where the condensation zone occurs; little operating flexibility exists for a given column. Consequently, the column diameter of the intermediate section must be particularly well matched to that of the absorber. The relationship of the intermediate section to the stripper, on the other hand, is not as restrictive. The pilot plant data show that a 4-in., rather than the existing 3-in.-diam intermediate section, would be better matched to the operation of the 3-in.-diam absorber. The combination column is being modified accordingly in preparation for the next test series. Higher solvent flow rates and correspondingly higher gas process rates will then be allowed.

Preliminary work is underway to evaluate various krypton purification options that will ultimately lead to the selection of the preferred final product purification train. The minimum acceptable product purity is 50% krypton. In view of the relatively large amount of xenon that has to be handled along with the krypton, one attractive option consists of a small combination column designed to effect a bulk krypton-xenon separation. Another option employs a chromatographic separation column. These two product purification schemes are currently being explored. Previously, xenon cold trapping was experimentally evaluated. The exact makeup and arrangement of this part of the process will be decided within the coming quarter.

3.5.2 Solid sorbent studies

R. T. Jubin

The cold shakedown runs of the solid sorbent test equipment were completed during this quarter. These runs led to several equipment modifications in an effort to avoid crystallization of iodine in the lines near the I_2 generator. One modification involved introducing the main air stream into the iodine-laden stream just as it exits the I_2 generator.

A leak at one of the Teflon flanges on the end of the I_2 generator during a cold iodine run led to a refabrication of the generator using glass-sealed ends. This modified generator also has two side ports for loading iodine and a coarse glass-fritted disk to separate the glass bead packing from a void area below.

Two runs have been made with a 2-in.-diam filter using an ^{131}I tracer (0.5 mCi) in a dry air stream flowing at 20 liters/min at a pressure of 5 psig, a filter temperature of 150°C , and containing a total iodine concentration of 0.00129 g/liter. During the first run, the

iodine did not break through the silver mordenite (AgZ) filter containing six 1-in.-long bed segments. Initial results are shown in Table 3.1.

**Table 3.1. Initial results of silver mordenite (AgZ)
filter iodine loadings**

Bed segment	Iodine loading (mgI ₂ /cm ³)	
	Run 1	Run 2
1	56.5	128.2
2	49.6	46.2
3	34.2	4.57
4	8.35	0.0795
5	0.257	
6	0	

The second run used only four 1-in. segments in the main filter. At breakthrough of the third segment, based on tracer analysis, the loading was as is shown in Table 3.1.

There appears to be a problem in assuring that the ¹³¹I is in equilibrium with the ¹²⁷I. In the second run, the feed gas exhibited a very high tracer content at the beginning of the run which rapidly decreased to about 10% of the initial value.

Portions of each filter bed have been submitted to the Analytical Chemistry Division to determine the total iodine concentration in the bed. This should indicate if the ¹³¹I is loaded in a constant ratio to ¹²⁷I.

3.5.3 Carbon-14 removal process development

G. L. Haag and A. D. Ryon

The development of processes for the removal and fixation of ¹⁴CO₂ released in the reprocessing of breeder-based fuels is being conducted with major emphasis on the treatment of high volumetric gas streams containing less than 1000 ppm CO₂. Processes under development include (1) the direct fixation on solid Ba(OH)₂ hydrate, (2) the direct fixation using a Ca(OH)₂ or Ba(OH)₂ slurry in an agitated gas-slurry contactor, and (3) carbon dioxide removal and enrichment using molecular sieves followed by fixation. The effects of gas flow rates, feed gas compositions, and various gas impurities on the decontamination factors (DFs) and final reactant conversions are being measured.

Ba(OH)₂ hydrate experimental studies. Major experimental emphasis this past quarter was directed toward the evaluation of additional Ba(OH)₂·8H₂O materials for CO₂ removal. Details of these experiments will be reported after patent applications are filed.

Analytical development. Two analytical developments were made this past quarter. A second Wilks/Foxboro Marian 1A infrared analyzer was received, installed in a glove box,

and calibrated. The capability now exists for the continuous on-line monitoring of two gas streams.

The second improvement involved the calibration procedure for the Baseline gas chromatograph also used for low-level CO₂ analysis. During normal instrument operation, the response of the flame ionization detector to methane concentration was found to be linear. The methane is obtained by the reduction of carbon dioxide over a nickel catalyst bed. Previous calibration curves were obtained using gas mixtures obtained from the Bureau of Mines Helium Plant Operation. This technique, however, was extremely time consuming. An exponential dilution system was then designed which would provide a sample gas with a concentration that would decrease exponentially with time. After numerous contamination problems, the system was found to be exponential in the 10 ppm to 100 ppb region. Therefore, with a clean carrier gas (ultra pure helium) and two reference gases, a calibration curve may be obtained. The major difficulty in developing this calibration procedure was the use of Teflon tubing which adsorbs appreciable amounts of CO₂. This problem was found to be more pronounced at low flow rates because of the time required to flush the system. The problem was eliminated by using copper and stainless steel tubing.

3.5.4 Integrated HTGR off-gas treatment system

R. D. Zimmerman, U. S. Park, N. G. Perreira, and R. D. Crabtree (General Atomic Company)

System shakedown was started July 2, 1979, and was completed July 31, 1979, as scheduled. All system flows, heaters, and heat exchangers were activated and controlled using the Diogenes process controller. All burner off-gas (BOG) system control loops and a part of the dissolver off-gas (DOG) system control loops were checked out during the system shakedown. The shakedown consisted of operating each loop first in manual control, using simulated inputs into the Diogenes process controller, then in manual control using real inputs, and finally in automatic control using real inputs. Integrated control with several loops operating in parallel was performed. In addition, all local mass flow control valves performed adequately.

Test procedures have been prepared for the first adsorption bed (SO₂) test. Test runs were initiated in August. During the next two phases, each component unit will be tested individually.

A regeneration system for the iodine and the iodine back-up beds has been added to the off-gas system. The system includes a recycle compressor, two heat exchangers, a heater, and a PbX adsorption bed. Regeneration of the iodine-loaded, silver-exchanged molecular sieve adsorbents is accomplished by desorbing the iodine with hot (500°C) hydrogen gas, which forms hydrogen iodide (HI), followed by adsorption of HI on the PbX bed at a lower temperature. Results from a laboratory-scale experiment at Idaho National Engineering Laboratory (INEL)³ show that the iodine desorption rate is a strong function of hydrogen partial pressure as well as temperature. In order to maintain a high hydrogen partial pressure, the system has to be purged before the hydrogen is recycled. Instruments and plumbing to monitor this purging process were also incorporated in the installation.

System insulation requirements have been estimated based on heat loss during both normal operation and regeneration. Nominal 75-mm (3-in.) and 50-mm (2-in.) insulation, with a thermal conductivity of 0.086 W m⁻¹K⁻¹ (0.05 Btu ft⁻¹h⁻¹°F⁻¹), will be required for the vessel and the lines respectively. All necessary materials (fiberglass insulation and ceramic cloth) have been procured, and installation is underway. The CO/HT oxidizer portion was completed during this report period.

The design work for system integration (the tie-in of the BOG and the DOG systems with the 0.2-m primary burner and the 0.5-m dissolver respectively) has been started. All required materials, including two compressors, have been ordered. The BOG compressor has been received. Completion of the physical hookup is expected during the next report period. Actual integrated process operation with the burner and the dissolver is not planned until next fiscal year.

The design of the radon (isotope 220) generator is underway. Equations to calculate the quantity of source material have been developed based on a multiple U-Th decay mode. The required quantity of source material depends greatly on the detection machine. Alpha detection requires a much smaller source than gamma detection. Inquiries are being made to identify suitable on-line alpha monitoring from radon daughter products.

3.5.5 Solvent mixture behavior studies

V. Van Brunt (University of South Carolina)

The goals of solvent chemistry research for the fluorocarbon selective absorption process are centered on a better definition of the ability of the solvent to absorb different gaseous species. Specifically, the establishment and confirmation of individual off-gas component solubilities in the fluorocarbon, the determination of the thermodynamic consistency of available solubility data, and the determination of mixture solubilities in the fluorocarbon are the research goals of the program at the University of South Carolina (USC). This research is an extension of two studies previously performed at ORNL utilizing radioactive tracers. Reliable, accurate, and thermodynamically consistent solubility data will provide a more accurate description of the mass-transfer driving forces in the ORGDP pilot plant. The individual and combination models of the equipment can be updated and this, in turn, will permit a more reliable scale-up design.

The experimental program at USC is to design, build, and operate a solubility measurement apparatus that can determine solubilities of the major off-gas components at the ORGDP pilot plant operating conditions [temperatures from -40 to 40°C , and pressures from 100 to 903 kPa (1 to 9 atm)]. The apparatus has been designed to provide sufficient data for more complete thermodynamic consistency analyses. It is contained within a constant-temperature air bath, designed to have liquid and vapor circulation with little energy input from the pump, and features liquid and vapor sampling by isolation rather than by withdrawal.

The basic components of the apparatus, shown in Fig. 3.6, include a primary gas-liquid equilibrium loop that contains the bulk of the gaseous and liquid species, secondary sampling loops, and temperature and pressure measurement subsystems. In the primary loop, liquid circulates from the bottom of the equilibrium cell, through the pump, and through an aspirator sprayer. The sprayer produces a fine liquid mist in the gas section of the equilibrium cell. A portion of the output from the pump flows through three liquid sample lines (one of which is shown in Fig. 3.6) before returning to the equilibrium cell. This liquid recirculation further induces mixing within the cell. Before equilibrium has been established, the Valco two-position gas chromatograph (GC) sample valves are set to permit recirculation. Once equilibrium has been achieved, the valve sample volumes are connected to a secondary sample loop containing a multiposition sampling valve that allows each sample to be analyzed by a gas chromatograph.

Fig. 3.6. Experimental apparatus for solvent mixture behavior studies. (Courtesy USC)

Vapor sample isolation is by a similar mechanism. Liquid flow through the aspirator provides a pressure drop (up to 15 in. H_2O) that promotes vapor circulation and mixing within the equilibrium cell. The three vapor lines recirculate the gas through three GC vapor sample valves.

Actuation of all six sample valves is by a single remote air pressure signal. This signal is transmitted only after pump action has been stopped and a quiescent condition has been established. It should be further noted that the vapor and liquid sample valves are physically located above and below the liquid level in the equilibrium cell, and that by taking three samples of each phase sample, measurement uniformity can be established.

Pressure and temperature measurement is critical for accurate thermodynamic consistency analysis of the data. Temperature measurement in both phases will be obtained using aged precision-calibrated thermistors. A two-stage quartz Bourdon tube assembly will be used for pressure measurements. The first stage is connected to the equilibrium cell and is contained within the constant temperature bath. Since there is the possibility of solvent condensation within this line, the secondary side of the first Bourdon tube contains dry nitrogen. It is connected to a Texas Instruments precision-calibrated quartz Bourdon tube assembly. The pressure is measured by a null pressure difference signal established between the equilibrium cell and the dry nitrogen, and accurate measurement of the dry nitrogen pressure using the calibrated tube.

The experimental program has included calibration and experimental operation of individual components of the overall experimental system. A thorough experimental program to establish the operating characteristics of the reciprocating magnetic pump was

performed. A graph of pump operation performance (Fig. 3.7) illustrates that even on the downstroke, a significant pressure difference is maintained through the pump, which is more than sufficient to drive the liquid through the aspirator, induce the liquid flow in the liquid sample lines, and induce the vapor flow in the vapor sample lines.

Fig. 3.7. Magnetic pump performance. (Courtesy University of South Carolina)

The purpose of the theoretical program at USC is to evaluate and modify an existing differential thermodynamic consistency procedure and to determine the thermodynamic consistency of all available fluorocarbon solubility measurement data. The Christiansen and Fredenslund procedure⁴ has been modified to reduce the number of empirical parameters and increase its accuracy. The Soave-Reclich Kwong Equation of State⁵ has been replaced by the Peng-Robinson Equation of State.⁶ This replacement increased the accuracy of phase equilibria predictions for highly nonideal systems and reduced the dependency on empirical coefficients. During the past quarter, the program modifications have been completely documented.⁷

3.6 Engineering Research Instrumentation Support

W. F. Johnson, S. S. Gould, G. R. Wetherington,
L. E. Ottinger, and G. V. Smith

3.6.1 Full-scale experimental voloxidizer

The four integral-orifice differential pressure cells that were installed to measure the cooling stack water flows were found to produce an excessively noisy output signal. This problem was remedied by installing a pressure reducing station in the cooling water supply header. A factor of ten reduction in water pressure established a fairly constant flow rate through the heat exchangers, and the system is now operational.

Panels containing 32 illuminated panel switches have been installed on the unit process controller to ease operator interface with the controller software.

The new ACCOL E software package has been compiled, debugged, and is now undergoing modifications to improve the communications between the unit process controller and the Autodata 9 data multiplexer.

Locations of the 33 drum thermocouples for the new temperature telemetry system have been designated. About one-half of these thermocouples have been fabricated, thermocycled, and x-rayed to establish the integrity of the junctions.

3.6.2 Small experimental voloxidizer

A communication network has been installed between the Engineering Research Unit Process Controller and all process substations utilizing this unit process controller. This communication capability should greatly enhance the operator interface and control tasks and expedite calibration of all the instrumentation.

A final checkout of the software package has been completed; all design requirements have been met. The controller has been turned over to the operating personnel.

3.6.3 Fluidic diode pump development

The functional keyboard/color CRT operator interface system has been debugged and placed into full operation at the Engineering Research Unit Process Controller Station.

All temperature and pressure transmitters have been calibrated and placed in service.

A cross-sectional calibration was completed on both feed and receiver tanks by the empirical construction of a differential volume per differential level profile for each tank. This calibration information was utilized in deriving proper constants to correlate level transmission data to actual flow values throughout the pumping system.

Installation of the stand pipe height control valves was completed allowing for final overall checkout of the pump stand instrumentation and control system. The pumping stand was found to perform well within design expectations and has been placed in operation.

Acknowledgments

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References

1. W. D. Burch et al., *Consolidated Fuel Reprocessing Program Progress Report for Period April 1 to June 30, 1979*, ORNL/TM-6994 (September 1979).
2. W. D. Burch et al., *Advanced Fuel Recycle Program Progress Report for Period April 1 to June 30, 1978*, ORNL/TM-6427 (September 1978).
3. T. R. Thomas et al., *Airborne Elemental Iodine Loading Capacities of Metal Zeolites and a Method for Recycling Silver Zeolite*, ICP-1119, Idaho Chemical Processing Plant, Idaho Falls, Idaho (July 1977).
4. L. J. Christiansen and A. Fredenslund, *AIChE J.* **21**, 49 (1975).
5. O. Redlich and J. N. S. Kwong, *Chem. Rev.* **44**, 233 (1949).
6. D. Y. Peng and D. B. Robinson, *Ind. Engr. Chem., Fundam.* **15**, 59 (1976).
7. L. L. Ham and V. Van Brunt, *A Thermodynamic Consistency Test Procedure Using Orthogonal Collocation and the Peng-Robinson Equation of State* (in preparation).

4. ENGINEERING SYSTEMS

M. J. Feldman

The scope of the work performed in the area of Engineering Systems spans the development of prototype equipment and the design of the Hot Experimental Facility (HEF). The design of the prototype equipment is based on other research and development efforts, primarily those of the Process Research and Development and the Engineering Research sections of the CFRP. These efforts include the development of individual equipment items and systems as well as their interaction between various equipment items in series. The Integrated Equipment Test (IET) facility provides for the synergistic testing of equipment and also the testing of the remote operation capabilities and characteristics of these components and systems.

The design of equipment and systems to be incorporated into the HEF will be derived from these developmental efforts.

The status of each of these efforts, including the conceptual design for the HEF, will be reported quarterly.

4.1 Engineering Analysis

M. J. Feldman

4.1.1 Study of reprocessing facilities at a nuclear energy center

M. J. Haire and D. C. Hampson

The data base developed by Exxon Nuclear Company, Incorporated, for the Nuclear Energy Center study was used to generate costs for reprocessing alternate fuel types in support of the Nonproliferation Alternative Systems Assessment Program (NASAP). Relative costs of reprocessing nuclear fuels were determined for eight fuel types, two reprocessing capacities for LMFBR fuels, and three reprocessing modes (i.e., flowsheets) for LWR-LEU (low-enriched uranium) fuel types. The estimated capital cost for the reference case (1500 MTHM/year of LWR-LEU) was 1043 million 1978 dollars, with an annual operating cost (including waste disposal and taxes but excluding recovery of prestartup costs) of \$156 million and a unit price of \$340/kg. The unit price calculation was based on NASAP economic assumptions and formulas. Only minor cost differences were determined between the various modes of LWR-LEU solvent extraction (e.g., coprocessing, full decontamination). Reducing the facility reprocessing capacity by 3 to 500 t/year reduced the capital costs by about 30 to 50%. Capital costs and unit price estimates for thorium-based fuels for light and heavy water reactors are about 1.8 to 2 times that estimated for LWR-LEU fuels. Costs for uranium- or thorium-based fast reactor fuels were about 50% higher than the corresponding fuel for light-water reactors. Table 4.1 gives a summary of capital and operating costs and unit prices.

**Table 4.1. Reprocessing cost and price ratios for alternative fuels
(referred to LWR-LEU fuel, with Pu fully partitioned and decontaminated)**

Case	Fuel	Rate (Mg/year)	Cost and price ratios		
			Capital	Operating ^b	Unit price ^c
1	LWR-LEU ^a	1500	1.0	1.0	1.0
2	LWR-LEU ^a	1500	1.0	1.0	1.0
3	LWR, U-Th	1500	1.9	1.7	1.8
4	LWR, Pu-U	1500	1.1	1.0	1.1
5	HWR, Pu-Th	1500	2.2	1.7	2.1
6	HWR, U-Th	1500	2.1	1.5	2.0
7	FBR, Pu-U/U/U	1500	1.5	1.5	1.5
7A	FBR, Pu-U/U/U	500	1.0	0.7	2.8
8	FBR, Pu-U/Th/Th	1500	2.5	2.4	2.4
8A	FBR, Pu-U/Th/Th	500	1.2	1.0	3.6
9	FBR, U-Th/Th/Th	1500	3.2	2.8	3.1

^aIn Case 1, U and Pu are partially partitioned in the 1B extraction systems. In Case 2, they are partially partitioned in the 1A extraction systems.

^bCosts exclude recovery of pre-startup costs.

^cCalculated by ORNL using NASAP guidelines and formulae for high risk industry economic parameters.

4.1.2 Thermal analyses of irradiated fuel subassemblies

M. J. Haire and C. A. Rhodes

Work has begun on the analyses of techniques for cooling irradiated fuel subassemblies in the head-end of reprocessing facilities. Primary emphasis will be on the evaluation of the fuel in the disassembly/shear system. This quarter, the literature was reviewed, existing capabilities were studied, and the extent of data and design method verification was determined.

4.1.3 Cost impact of remote maintenance on fuel reprocessing plants

D. C. Hampson

Science Applications, Incorporated (SAI), Richland, Washington, is conducting a one-year study of the cost impact of remote maintenance in fuel reprocessing plants. The study objective is to identify which remote maintenance operations meet the current design requirements for a licensable reprocessing plant and to evaluate the cost effectiveness of these options in a commercial plant.

This study had been divided into six tasks and a description of each task was reported previously. The final reports for each section have been completed except for the summary report, which is in draft form.

4.1.4 Pyrochemical reprocessing study

D. C. Hampson, E. H. Gift, and O. O. Yarbrow

The final draft report is being revised for publication.

4.2 Component Development

E. D. North

The Component Development effort is a follow-on to that of the Engineering Research. The Component Development mission is the design, fabrication, and demonstration of the performance of pilot-plant chemical process equipment as designed for remote operation and maintenance.

The dissolution task is active at this time. It is anticipated that the tasks of solvent extraction, feed preparation, and product conversion will be activated in the near future.

4.2.1 Dissolution

J. Q. Kirkman

The Component Development effort in the dissolution area is directed toward the designing, constructing, and testing of a 0.5-t/d pilot-plant-scale dissolver system. This unit consists of a remotely maintainable rotary dissolver integrated with the support equipment that is necessary to produce a functional dissolution system.

Prototypical rotary dissolver. Major activities this report period have included performance of dissolution system tests utilizing chopped iron rod, investigations into the response of the dissolver liquid outlet concentration to step changes in inlet flowrate and in inlet concentration, and initiation of a conceptual design for an equipment system to process hulls and fuel element scrap exiting the dissolver.

The dissolver dissolution testing during this report period involved runs using chopped iron rod (0.64-cm-diam by 2.5-cm-long) as a stand-in for heavy metal feed. Sheared stainless steel tubing was also fed to the dissolver to simulate fuel element cladding.

The most significant iron rod test was a 32-h continuous run. In general, the dissolver operated satisfactorily throughout the run, however, a number of difficulties were encountered in the support equipment and systems.

It was observed during this testing that the use of iron rod produced a much more controlled, subdued dissolution reaction as compared with the vigorous reaction produced by the use of powdered iron runs that were described in the last quarterly. Although the dissolver pressure fluctuated in the iron rod test, as it had during the powdered iron testing, specific changes in the off-gas control system greatly improved the situation.

Review of data from the continuous iron rod test indicated that approximately 6 h were required for the dissolver liquid outlet to reach steady-state concentrations of ferric nitrate and excess nitric acid. Chemical analysis of the dissolver steam generator showed only trace amounts of nitric acid and iron, indicating that the previously encountered "dissolver drum leak" was not occurring. Finally, periodic checks of the liquid clinging to the rinsed stainless steel hulls leaving the dissolver showed that the liquid was about 1.5 M HNO_3 , but contained only trace amounts of iron. These results indicate that all the iron was being dissolved in the drum and was recovered in the liquid product stream.

In addition to the iron dissolution runs, two tests were conducted to investigate the dissolver liquid outlet behavior in response to transients in flow rate and concentration in

the inlet stream. In the first, step changes in inlet flow rate were introduced into the dissolver at three separate drum rotational speeds. Continuous monitoring of the liquid outlet flow rate indicated that steady-state flow was attained about ten minutes after the inlet step change was initiated. The second series of tests was more complicated and involved simultaneous step changes in inlet flow rate and inlet acid concentration. In general, the outlet acid concentration responded slowly, taking from 2 to 2.5 h to reach the steady-state concentration established by the inlet flow rate and concentration. Analytical modeling of the dissolver liquid outlet response to inlet transients is presently in progress (see Sect. 3.2).

Finally, engineering work directed toward developing a conceptual design for a hull handling system at the dissolver exit was initiated. This system is required to collect the stainless steel fuel element material (hulls, wires, shroud) that is discharged from the dissolver and to wash, rinse, dry, and deliver the material to the waste handling system for nondestructive assay. Progress on this conceptual design will be reported in future reports.

Dissolver support systems and process equipment. The necessary support systems have been integrated with the rotary dissolver to form an operable dissolution process. These support systems include a feed system, a product collection system, a product clarification system, an NO_x scrubbing system, and a digital control system. The flowsheet describing the dissolver support system was presented in previous quarterly reports.

Performance of the dissolver support systems and equipment during the 32-h continuous iron rod dissolution test encountered some difficulties. First, the test was interrupted for about 30 min while the motor of the vibratory feeder was replaced. (This feeder meters the iron rod and the stainless steel hulls to the dissolver.) Second, automatic data transmission and recording were lost when the CODEDACS computer system failed (cause undetermined) midway through the run. Dissolver data storage was shifted to a local teletype terminal for about 1 h while the CODEDACS system was brought back on-line. The local digital process controller, providing control for the entire dissolution system, was not affected by the CODEDACS failure and continued to function well throughout the test. Third, the on-line instruments for measuring dissolver off-gas density and NO₂ concentration failed, due to excess moisture in the gas sample lines. The standard practice of periodically withdrawing gas samples for laboratory chemical analysis minimized the effect of the loss of these instruments. Due to the failure of the connecting pin between the valve operator and yoke, the dissolver product solution diverter valve failed late in the run. This valve directs dissolver outlet solution to one or the other of the two product digestion tanks. The failure prevented shifting the flow from the full on-line tank to the empty standby tank and resulted in the test being terminated.

Dissolver instrumentation (D.M. Fleischer, W. F. Johnson, J. A. McEvers, and G. R. Wetherington, Jr.). Instrumentation efforts of this period were centered on improving primary sensor accuracy, modifying the digital process controller to increase flexibility, and developing several data reduction algorithms.

Primary sensor work has involved carefully calibrating various flowmeters in the system, adjusting density and level pressure transmitters, and checking the accuracy of temperature transmitters. Improvements in this instrumentation have substantially increased the accuracy of dissolver system material balance calculations.

Software changes in the system digital process controller have improved the control of the dissolver steam generator, provided an airlift control loop for the recycle acid system, filtered noise from process density signals, minimized dissolver pressure fluctuations, and provided automatic numerical integration of all dissolver system flow streams.

Two programs were written; one to recall dissolver data from tape to simulate real-time conditions, the other to plot data. Both are presently being debugged. A program performing real-time material balances, which utilizes process data transmitted from the dissolver to CODEDACS, was in operation during the 32-h continuous iron rod dissolution test (Sect. 5.2).

4.2.2 Solvent extraction

J. Q. Spencer and M. E. Hodges (Savannah River Laboratory)

The HEF flowsheet shows a centrifugal high-activity (HA) contactor. A modified Savannah River centrifugal contactor is being designed and is to be sized for use in the HEF. This type of contactor will be installed and cold tested at SRL.

Planning began for the centrifugal contactor test facility to be installed at the semiworks at SRL. Equipment is being designed to provide sufficient capacity to operate a bank of 0.5-t/d contactors up to 18 h without recycle. The facility will have the flexibility to run tests with cold chemicals and natural uranium on either a simple 10-t/d contactor or a bank of 0.5-t/d contactors.

An on-line colorimeter was obtained and will permit real-time study of concentration changes and an approach to steady-state operation. This instrument consists of a remote probe connected to a light source and detector by a fiber-optic cable.

4.2.3 Feed clarification

J. D. Spencer, S. F. Peterson, and G. C. Rodrigues (SRL)

Work on the task of feed clarification in the HEF has begun and is required to (1) recover dissolver solids for additional dissolution of insoluble plutonium and (2) remove solids from the feed to the centrifugal HA contactor.

Head-end feed clarification for the HEF is being reviewed with sources for the review to include Savannah River Plant (SRP) experience, SRL experimental work, DOE programmatic references, and other literature. The SRP experience will be of little value because of the low burnup of fuels typically processed there. These sources relevant to clarification processes in the HEF indicate that centrifugation alone, as planned for the HEF, may be insufficient. The use of a flocculating agent should help, but this must be tested under the high-shear conditions that are found with a continuous-feed centrifuge. Flocculation may also work with simple quiescent settling. Another viable process may be filtration with or without flocculation. Filter aids may also be used.

4.2.4 Component development data acquisition and control system

J. A. McEvers, R. M. Tate, and R. W. Tucker, Jr.

The data acquisition and control system in support of the component development activities consists of the following :

1. a Digital Equipment Corporation PDP 11/40 central processing unit (with 128 K of memory);
2. two 9-track, 800-BPI, 45-IPS magnetic tape drives;
3. six 1.2-megaword disk drives;
4. a 300-line/min line printer;

5. a 30-character/s hardcopy terminal, which serves as the system console;
6. two Tektronix 4006 graphic CRT terminals;
7. 64 channels of analog to digital converter equipment;
8. several digital input/output channels.

Also provided are communication facilities that allow the system to receive and transmit data in serial ASCII form (to and from remote terminals and equipment). One such piece of equipment is the Bristol UCS-3000 process unit controller (PUC).

CODEDACS is currently being used to receive, store, and list data that are obtained from the instrumentation attached to the dissolver and transmitted to the system by a Bristol PUC. The data are stored on magnetic tape for further processing (if desired) and are also available directly from the computer's memory in near real-time (limited to the frequency of transmission from the Bristol PUC) for such purposes as real-time material balance determination and process monitoring. The plotting software to be added soon will provide both the capability for plotting near real-time data and data stored on magnetic tape.

The analog to digital conversion facilities and the digital I/O facilities are used to gather data from the 200-ton Birdsboro shear and to control the operation of the shear, via a programmable logic controller (PLC). This portion of the system has been designed to allow CODEDACS to exert control over the PLC, which controls the sequential operation of the shear, and to perform the acquisition and storage of data obtained from instrumentation that is attached to the shear. The data stored on disk may be plotted immediately to provide a graphic display of the shear compactor position, compactor pressure, compactor horsepower, ram position, ram pressure, and ram horsepower.

The system has recently demonstrated that the shear operation can be started and stopped by the CODEDACS, that data can be collected in real-time (under manual control), and that the data can be plotted graphically on one of the Tektronix 4006 terminals.

Seven of the eight major software components, which were designed for the system, have been completed and are being tested. The last component is responsible for the automatic coordination of the shear operation, with the data acquisition operation, and requires the determination of actual shear-control-signal sequencing prior to completion. This work is presently being performed.

4.3 Systems Development

N. R. Grant

The Systems Development work is directed toward the development of the major components and the systems that are closely associated with the operations and maintenance aspects of the HEF. All of the tasks are primarily mechanical in nature, that is, not part of the chemical process. The goals of Systems Development are the design, fabrication, and operation of full-scale remotely operated equipment.

Prior to this reporting period, the tasks assigned to this area were the Integrated Equipment Test (IET) facility, the receiving and storage systems, the special remote systems, the remote control engineering systems, the waste handling systems, and the procurement of depleted uranium fuel to be used for tests, equipment, and process development. During this reporting period, two other tasks were moved from the area of Component Development to this functional group. These are the disassembly and cutting task and the voloxidation task.

4.3.1 Disassembly and cutting

S. A. Meacham (Westinghouse Advanced Reactors Division), E. C. Bradley, D. K. Lorenzo, B. S. Weil, and W. F. Johnson

The Systems Development effort in disassembly and fuel cutting is responsible for the mechanical preparation of the fuel materials for the succeeding steps of voloxidation and dissolution. To accomplish this, the task expects to develop equipment that will remove the undesired components, such as inlet and outlet nozzles, from the fuel assembly and that will cut the remaining portion of the assembly into short pieces. The sheared product will expose the contained fuel for subsequent oxidation (in the voloxidizer) and leaching (in the dissolver). The goal of the task is to produce the necessary design, equipment, and data required for successful operation of similar equipment in the HEF.

Systems integration.

ROMD/IPD equipment integrated study. A ROMD/IPD equipment integrated study (installation and operation) was performed. Three basic scenarios were developed which were structured around a FY-1985-need date for design information of the HEF equipment. The basic difference between the three plans is centered around whether the total equipment integration takes place in ROMD or IPD and when integrated operation would start at the given location. Information for cost and scheduling has been prepared.

Quality assurance assessments. A quality assurance assessment plan (QAAP) for the disassembly and cutting task has been prepared. The basic plan is to assess the overall task (level 0) and then to perform subtask assessments as required (level 1). Activity assessments (level 2) would be conducted as determined by the level 1 assessment. Quality assurance assessments for two major items of equipment, remote shear and disassembly machine, were also prepared. Each assessment addresses the four phases of work to be accomplished: advanced conceptual design, final design, fabrication, and installation.

Disassembly systems.

Disassembly machine (D. M. Fleisher). The conceptual design requirements document for the disassembly system has been approved. The system's equipment integration study has been initiated (Sundstrand Energy Systems).

An updated I&C section was prepared for inclusion in the disassembly systems design requirement document. Changes were made to allow the use of a PLC in the control system design, to indicate the incremental feed speed that may be required by the shear, and to require that an analog signal representing fuel position be transmitted to the remote shear.

Plasma torch development (G. R. Wetherington, Jr.). Testing continued on the plasma torch cutting system during this quarter. The variables which appear to have the most influence on the cut quality are assembly rotation speed, nozzle size, nozzle power, and cut gas flow rate. Thus far, water injection cutting, using about 700 A of current, has produced the best results, that is, no welding of the rods to the shroud and minimal slagging of the rods to each other. The tests performed also indicated that the dummy subassemblies containing solid tool steel rods may not be an appropriate simulation of the solid stainless steel end plugs. Stainless steel appears to give more desirable cut characteristics, that is, less slagging and welding, than does the tool steel. In addition to the melting point and specific

heat, apparently some other parameters, such as the high-temperature behavior of chromium, are significant. All future tests will be performed on the stainless steel rods that were delivered this quarter.

A feasibility experiment of transverse cutting was performed during the latter half of July. In this approach, the subassembly remained stationary while the plasma torch moved across the cut plane. This eliminated the circumferential-cut problem of metal being blown back across previously cut rods and welding them to the shroud and to each other. This method of transverse cutting produced cuts of comparable quality to the best of the circumferential cuts. Based upon these encouraging results, an improved mechanized transverse-torch positioner was designed. Further experimentation is planned.

Instrumentation and control testing of radiofrequency interference on potential nearby in-cell equipment has continued to produce favorable results except for temperature transfer, which showed a 20% increase in signal level during the cut. A temperature controller showed no interference effects. The closed circuit video transmitter was also essentially unaffected, although some static was observed. The final tests will be performed using a digital controller next quarter. Instrumentation to measure and record the actual amperage and power use during a cut was installed and calibrated. A timer was installed to measure the actual arc duration.

A Bristol USC-3000 unit process controller and a KIM (a microprocessor development package) have been installed in the 7608 area (near the plasma torch) for rf interference tests. These tests should be completed next quarter.

The plasma torch experimental plan was revised to increase the scope of the work and to reflect the additional time and money needed for completion of the revised program. Testing is now scheduled to conclude in January 1980.

Laser cutting development. Two specimens of zinc selenide (laser window material) and two metal mirrors received a total dose of 2.35×10^8 rads last quarter in the ORNL ^{60}Co irradiation facility. The metal mirrors were not affected by the radiation. The specimens of zinc selenide showed considerable change in their appearance. The uncoated sample was slightly darkened, while the sample with an antireflection coating had a dendritic pattern on one side.

Laser optical materials were sent to Argonne National Laboratory this quarter for ^{60}Co irradiation. The test sets consisted of two groups of coated zinc selenide and of two groups of metallic mirrors with a copper, a molybdenum, and a tungsten mirror in each group. Maximum dosage for each zinc selenide group will be 10^7 and 10^8 rads respectively. The total dosage for each of the two mirror groups will be 10^9 and 10^{10} rads respectively.

The laser cutting tests at United Technologies are nearing completion. The tests were conducted to evaluate cutting parameter tolerances, to determine the effect of laser cutting on material at elevated temperatures, and to establish basic cutting parameters for removing end hardware from LMFBR- and LWR-type fuel subassemblies.

Laser cutting tests have been conducted on shroud material (type 316 stainless steel) at elevated temperatures (149, 315, and 538°C). cursory examination of these sample cuts indicates that there is little or no difference in the cutting characteristics or in damage to the ceramic-filled tube at 149°C relative to the results at room temperature. At 315°C and 538°C, however, the laser beam penetrates farther into the ceramic material. Parameters to prevent penetration of the simulated fuel pin are being established.

A focus head and follower demonstration unit has been built and checked. Both passive and active guidance systems have been employed in a laser focus head that demonstrates reasonable remote maintenance features. Detailed testing of the unit will begin next quarter.

An analysis of optical control techniques for laser system guidance began this quarter, and a review of reactor fuel designs amenable to laser cutting was initiated. The fuel designs being reviewed are those of the CRBR, FFTF, PLBR, GCFR, and PWR.

Shear systems

Allied-General Nuclear Services (AGNS) shearing study. The final draft has been approved and transmitted to AGNS for publication. This completes this activity.

Remote shear development (L. E. Ottinger). The report prepared for the remote shear concept provides clarification of the logic and analysis leading to the selection of the remote shear concept and relates how various features have been incorporated.

Work on the out-of-cell water-hydraulic system was initiated this month with the Planning Research Corporation (PRC). The system features a dual-fluid system that eliminates contamination of the pumping system and prolongs the life of the pump. This concept is considered a valuable addition and will be incorporated in the design. In addition, a trade-off study was conducted to determine the optimum pump size versus shear cycle time, and a draft report of the overview study of applicable hydraulic systems for the HEF was prepared. The I&C portion of the hydraulic control system was also reviewed and the interface requirements were identified.

The water-based hydraulic fluid irradiation study has been initiated to determine the effects of a radiation environment on the hydraulic fluid that is proposed for use with the remote shear. The results of the study will be used to assess the effects any radiation-induced changes in the fluid will have on the equipment. Also, the useful life of the fluid and the expected frequency of maintenance will be determined. The instrumentation requirements for the hydraulic system/power package have been prepared.

The logic flowsheet is being upgraded to include the operation of the vertical restraint, and the initial layout has begun on a process flowsheet.

Communication methods are being developed for interfacing a programmable logic controller (PLC) to a computer terminal for writing and modifying the PLC programs.

Possible shear display techniques on a CRT are also being investigated. There is a proposed layout of the display for the jammed shear condition. Measured values of the positions and the maximum hydraulic pressures will be presented for the shear, gag, and compactor along with a graphic display of their relative positions. The component position display will offer six levels of magnification for X1 to X32, with a maximum resolution of 0.0047 in.

The high-pressure remote connector study package has been placed with Aerojet Manufacturing Company.

Birdsboro shear (F. Sweeney, C. M. Smith, and D. N. Fry). Effort continued this quarter on the preparation of the topical report regarding the shearing studies. An evaluation of the various tooling designs and their respective performance regarding product character is currently being performed.

Analysis of the tape recorded fuel bundle shearing data has been completed. Criteria for the broken blade detection package is being formulated from the experimental data. Development of the compactor analysis package is continuing.

4.3.2 Prototypic voloxidizer

J. E. Van Cleve, Jr.

The subcontract with Nuclear Systems Associates, Incorporated, to perform a third-party review of the prototypic voloxidizer design, was completed. The review showed

that the design did comply, in general, with the criteria. Potential problem areas were identified and solutions suggested. These study results will be incorporated in the succeeding design work.

A number of ways to accomplish the design and fabrication of the prototypic voloxidizer within limited funding have been considered and three options were selected for further consideration.

4.3.3 Integrated Equipment Test (IET) facility

J. G. Stradley, H. W. Harvey, J. B. Kendall (Exxon Nuclear Company, Incorporated), and E. L. Nicholson

The IET task consists of modifications and additions to the CFRP complex (7600 area). These modifications will provide an experimental area where performance and remote operational and maintenance capabilities for reprocessing equipment and systems can be developed. The IET task is comprised of three basic phases. The first phase established an area where specific pieces of process equipment can be operated as an integrated system. These are equipment components that have evolved from the developmental efforts. This portion of the IET facility has been designated as the Integrated Process Demonstration (IPD). The second phase of the task, the Remote Operation and Maintenance Demonstration (ROMD), provides the facilities and equipment necessary to develop remote maintenance capabilities and philosophy for the equipment of the CFRP. The third phase is designated as the General Plant Facility (GPF) and consists of structural modifications, utility system expansions, and construction of ancillary facilities, all of which are required to house and support the IPD and ROMD experimental programs. The status of the Title II design for the three phases is as follows:

1. The IPD design effort (without the Iodex system) is slightly behind schedule (84% actual vs 88% scheduled). Design has continued on the Iodex and magnesium nitrate systems.
2. The design for ROMD is on schedule with 91% complete.
3. The General Plant Facility design is complete and a contract has been awarded for the required work. The contractor started in July and completion is scheduled for May 1980.

Integrated Process Demonstration. The tanks, heat exchangers, evaporators, piping, and other IPD equipment items furnished by the line-item are being procured by UCC-ND for installation by an outside contractor. Title II design is complete and procurement is in progress for all the major pieces of equipment except the Iodex system.

Bids on the distributed data acquisition and control system (DDACS) are under review. It is anticipated that a contract for this system will be awarded in November. Design of the piping and instrumentation and the preparation of the installation specification is underway.

Remote Operation and Maintenance Demonstration. The contract for the integrated crane and manipulator system was let in August.

The designs of the remote shielding walls, horizontal transfer devices, master/slave manipulators, periscope, remote mirrors, and television system were approved and released for procurement. The gantry bridges were delivered in July and are to be installed by the GPF contractor for use in the installation of manipulator systems.

4.3.4 Receiving and storage

S. A. Meacham (Westinghouse Advanced Reactors Division) and E. C. Bradley

Nondestructive assay. The assessment study of the nondestructive assay (NDA) mechanical system was completed by Sunstrand Energy Systems. The study was to determine the equipment development approach that would satisfy the requirements identified in the scoping study. The primary approach includes the equipment to perform the fuel handling functions, positioning of the neutrons source, and neutron detector cooling and replacement. The results of the study will be reported next quarter.

Sodium removal. Proposals from three vendors on the sodium removal experiments program were received and evaluated. Westinghouse was selected to perform the experiments. A rough draft of the experimental test plan has been prepared for ORNL review. The design of the subassembly models has been completed and fabrication has begun. The model design is dimensioned to give a prototypic CRBR pin-to-pin gap of approximately 0.05 mm, and incorporates prototypic type 316 stainless steel cladding, end caps, wire wrap, and rail materials.

Storage. The WARD/ORNL corrosion III experimental program, exposing prototypic irradiated cladding specimens to water, has been completed. Some of the specimens showed evidence of corrosion. Six of the specimens were selected for metallurgical examination at LASL, and the remainder will be included in an extended water exposure program of an additional eight- to ten-month duration. Following completion of the extended program, all of the remaining specimens will be examined metallurgically for signs of corrosion.

4.3.5 Special remote systems

R. Blumberg and W. F. Schaffer, Jr.

The objective of this task is to develop special remotely operated systems that are not assigned to other Systems Development tasks. The need for development of one of these systems is established by the requirements of the HEF conceptual design or by other tasks in Component or Systems Development. There are three systems currently being studied: remote connectors and jumpers, remote welding, and sampling.

Remote connectors and jumpers. Improvements in remote connectors are being developed for use in the HEF. Existing technology consists principally of the Hanford-type connector, which has been used extensively in several nuclear fuel reprocessing plants. This connector, which we consider as the reference design for the HEF, utilizes a Teflon seat and can be operated by a crane and an impact wrench. The development program is proceeding in parallel paths; the modification of the Hanford design to accept a radiation-resistant seal and the development of other designs that may offer additional improvements. The development program consists of four areas of activity. These include modifications to the Hanford connector to replace the original Teflon seal with a radiation-resistant seal, the design and procurement of connectors that offer alternatives to the Hanford design, the remote handling tests, and the seal performance tests. There has been no significant progress on the first three of these activities; therefore, only the last activity is reported here.

Seal performance tests. The connector environmental test stand (CETS), which will be used to qualify seal performance under a set of controlled environmental stresses, is being procured. The largest component, consisting of a massive frame capable of resisting the mechanical stress to be imposed on the connector and the machined fittings, was delivered

in mid-September. The balance of this procurement is scheduled for delivery early next quarter, and an assembly and installation effort is to begin soon thereafter. In addition, the program for controlling the testing has been written and debugged on hardware similar to that being procured for the facility.

Remote welding. The ability to cut and reweld pipes in the process systems environment of a fuel reprocessing plant would, in many instances, provide a useful substitute for remotely operable disconnects. A development program has been started to provide this capability for one specific application in the HEF; namely, the interconnecting piping. This is the piping that interconnects the process modules and joins the process to the off-gas system. A large number of remotely operable disconnects could be eliminated through remote welding capability. The resulting all-welded piping would not only cost less in the initial installation, but it would also be much more reliable by requiring less maintenance.

A development program has been started at Battelle Columbus Laboratories for a preliminary study on equipment requirements for welding in a remote environment. There are two aspects of this study that are unique.

1. The hot-cell environment is to be emphasized. This goes beyond the work previously done in the commercial field of automatic welding where many operations are still done manually.
2. The overall process is to be considered. Producing a weld requires many operations such as cutting, joint preparation, alignment welding, and inspection; all of these steps are essential to this process.

The study was started in September and is scheduled for completion in six months. A conceptual version of the remote welding is shown in Fig. 4.1.

Fig. 4.1. Conceptual version of the remote pipe welder.

Sampling system. An automated liquid sampling system has been accepted as the reference system for the HEF. The major activity in this development program is being conducted by Los Alamos Technical Associates (LATA); a preconceptual study is scheduled to be completed soon after the end of this quarter. The objectives and results of three areas of the study are as follows:

1. Objective: To determine a method or methods of filling the sample bottles by means other than a pair of hypodermic needles. Results: It was determined that a nozzle with an inner bore and an outer annular passageway would serve this purpose. There are both advantages and disadvantages to this approach. A test program has been started to refine the nozzle design and the operating technique and also to evaluate the performance of the nozzle. The major potential benefit expected is a very large increase in reliability over the usage of the needles.
2. Objective: To compare alternative methods of needle block and sample station maintenance. Result: A comparison between a manipulator-held maintenance tool vs a maintenance system mounted on the sampler vehicle concluded that the former system was much more desirable. Various methods of connecting the service lines to the sampler station were also studied.
3. Objective: To determine the specific interfaces of the sample system with the HEF. Result: The most involved and complex interface is the determination of the space envelope required for the structural mounting of the track and sample station. The information was developed by providing the latest HEF layouts in the area where the sample stations were to be located and by designing the structure of the vehicle, sample station, and the track. An elevated cross section (Fig. 4.2) shows the vehicle configuration as required by the HEF.

As part of the design effort, several subsystems were investigated: the electronics control package, shielding requirements, the propulsion/suspension system, the station location system, the data communication link, the item identification system, and the operational duty cycle.

Program plans for the continuation of the sampler system have been prepared. Subsequent steps will be directed toward the design and fabrication of a full-size development-oriented, prototype vehicle that can be installed and operated in the ROMD.

Instruments and controls effort (B. J. Bolfig). During this reporting period, considerable progress was made in defining the on-board control system, its interfaces, and its modes of operation. The area of radiation effects on electronic components was reviewed in terms of the dose levels that the various electronic components could take, which components could be "hardened," and which components showed promise for future improvement of either being hardened or further miniaturized. Although this information is preliminary, it was used as a basis for a trade-off study on control systems. From this, decisions were made regarding the shielding that is to be installed on a prototype vehicle.

The on-board control system is now configured with a microprocessor (programmed in assembly language) that will control individual actuators on a one-at-a-time basis. This simplifies the electronic system and its operation. The vehicle will communicate with an operator station over a wireless (radio frequency) link. The operator will be able to command either individual actuations or sequenced operations. This is required for checkout and development of the system. An instrumentation schematic superimposed on an isometric view of the sample vehicle is now approximately 40% complete.

Fig. 4.2. The ATLS sampling system.

4.3.6 Remote control engineering

J. Garin (Westinghouse Advanced Reactors Division) and B. J. Bolfing

The remote control engineering task was established to improve the technology for remote control and manipulation systems in the radioactive environment of nuclear fuel reprocessing plants. The primary goals of reducing personnel exposure and the requirements for in-cell man access can be obtained by the upgrading of current remote system technology. These improvements are aimed at making the remotely controlled systems more reliable, more easily maintained, and more efficient, thereby increasing overall plant efficiency. Due to changes in the evolving design of the HEF, increased emphasis is being placed upon electrically driven master/slave manipulators which provide increased dexterity.

Electromechanical systems (K. Sharp and P. E. Satterlee). This subtask is involved with the improvement of signal and power transmission to and from the manipulator transporter systems, overhead and on the cell floor. This equipment includes remotely operated bridges, carriages, hoist, floor transporter, and manipulator systems. The controls for these systems and the communication between the in-cell equipment and operator are being demonstrated as a system in TURF cell E.

A PDP 11/34 minicomputer has been interfaced to the three-axis microcomputer-based overhead handling control system for implementation of teach/playback and obstacle-avoidance functions. The interface has been debugged in the laboratory and is completely operational. The minicomputer is installed in TURF. All necessary cables have been fabricated, and a circuit has been installed for the computer.

The first set of software routines has been developed, debugged, and documented to implement teach/playback on the new minicomputer. These routines allow the operator to store set points on the system's mass storage device and to play back the set points. Using these routines, the operator may combine set-point sequences into a longer sequence, delete set points from any sequence, and list set points on the terminal.

Work has begun to convert a PaR-3000, six-degrees-of-freedom arm from switch-box-rate control to closed-loop, computer-based position control. A first draft summary of the system design requirements has been prepared and is being reviewed. A commercially available digital multiplexing system has been identified for telemetering communication of the manipulator arm sensor and the command data.

A simple wireless signal telemetry system is being breadboarded for laboratory testing of an inductive loop signal transmission scheme. The data transmission capabilities of the system will be investigated by sending and receiving data on already installed loop antennas. The advantages of this system over the optical signal transmission link presently used in the TURF cell E overhead handling system include reduced alignment problems and elimination of the need for radiation-hardened optics, and the system is thought to be immune to in-cell signal reflections.

Viewing system (D. Bible). Purchase specifications for a miniature TV camera, TV viewing monitors, and a pan-and-tilt mount have been completed. This equipment is to be installed in TURF on the camera mount that is currently being designed with controls for the mount as specified.

A study was initiated with the University of Florida to develop methodology for hand/eye coordination on the integration and optimization of closed circuit TV (CCTV) viewing systems and the manipulator controls. This study will lead to the conceptual design of an improved man/machine interface control system. The equipment specified will be used in experiments to demonstrate the required CCTV.

Servomanipulator development (S. Gould). The procurement of a commercially available servomanipulator system has been initiated. Bids have been received and are currently being evaluated. It is expected that a contract award will be made by mid-October.

The Brookhaven master/slave servomanipulator system is currently being reactivated. The system's servo amplifier electrical control package has been checked and repaired; the arms position and force transducers have been repaired; wiring harnesses have been repaired and modified as necessary; and replacement torque motors, position transducers, and power supplies have been ordered for future maintenance of the manipulator arms. Final servo loop tuning, calibration, and checkout is proceeding. This system is being reactivated to alternate experiments with the control system so that preferred control methods may be determined.

A draft of a specification for an advanced servomanipulator system is complete. The specification includes the required features that are applicable and unique to the HEF.

Remote maintenance studies. The study for an advanced electromechanical handling system (the rigid hoist articulated grapple) is 60% complete. Some key items that have been completed include a detailed study of the control system; the configuration of the boom that positions the manipulator at the work place; an actuator design, an innovative pancake motor, and a revolute gearing system; and an interim report (issued in July).

4.3.7 Waste handling

J. E. Van Cleve, Jr. and D. K. Lorenzo

The selection and/or development of methods for the conversion of all of the different radioactive wastes of a fuel reprocessing plant (HEF) into an acceptable, containerized product ready for shipment to a federal repository is the basic requirement of this task. As reported previously, this task will follow waste development work of other laboratories, provide our input where our unique problems are not fully investigated, and adapt resolutions to the HEF design. In the areas where little or no development is being performed, such as metallic waste packaging, this task will follow through on all of the equipment phases of scoping studies, design, fabrication, and testing.

The major activity has been the instrumentation and controls work in developing a leached hulls monitor technique. Work has progressed through experimental confirmation of the active neutron interrogation method of analysis. The scoping study report, to be issued in the next quarter, showed the validity of this method to meet the system's requirements. Meetings were held to resolve the requirements of the system and involved all disciplines interested in the monitor. The results of these meetings, along with previously developed ideas, are being incorporated into a criteria document to be issued in early October.

4.3.8 Uranium for tests

N. R. Grant and R. W. Knight

This task is divided into three areas: (1) the procurement of dummy assemblies as feed material for the disassembly/shear tests, (2) the procurement of depleted uranium dioxide as feed material for the voloxidizer and/or the dissolver, and (3) the disposal and/or recycle of uranyl nitrate. Only the first area had reportable progress this quarter.

Ten of the 20 dummy assemblies ordered from a vendor have been delivered. The completion of the other ten units has been delayed by fabrication problems in the manufacture of hex ducts from type 446 stainless steel. The vendor believes that fabrication problems will be resolved by using spinning and expansion techniques rather than the commercial draw-bench method used for 300 series stainless steel. The other ten assemblies should be completed and shipped by late October. The fabrication problems have also postponed the date of exercising the option to manufacture the FY 1980 order from October 1 to December 1. The vendor has requested the extension so that the impact of the duct fabrication problems on subsequent work may be fully evaluated.

4.4 HEF Conceptual Design Study

J. R. White

The revised arrangement of the process building that will be used as the basis for the HEF Conceptual Design Report (CDR) has been established and building drawings are being

prepared by the Architect-Engineer (Bechtel). This new arrangement has resulted in a significant reduction in the size of the process building as compared to earlier concepts, and it provides an improvement in the safeguards features.

Concept studies for the remote manipulator transporter, process module disposal, cell ventilation, and automatic sampler systems are nearing completion. These studies are being performed by subcontractors who specialize in the design of complex electromechanical systems.

A wooden model that simulates the most complex features of a typical process module has been fabricated. This full-scale model will be shipped to the Los Alamos Scientific Laboratory (LASL) for functional evaluation of the remote maintenance features using LASL's electric master/slave manipulators.

A tritium fractionator system has been designed for use when thorium fuels are processed. It is anticipated that voloxidation will be ineffective in releasing tritium from thorium fuels, and a supplemental system will be required.

4.4.1 Site and support buildings

O. A. Rogers

Site and support building criteria documents have been summarized in revised format initial draft with a few exceptions. Criteria relating to the communication systems cooling tower and site monitoring will be completed during the next quarter.

Bechtel prepared two layouts for a spur rail. The routes are being studied and costs will be estimated. One route is through the Oak Ridge Gaseous Diffusion (K-25) Plant, the other passes east of the K-25 plant. A study to determine the viability of the first route has been deferred until a more firm decision is obtained on the HEF site selection.

The secondary fuel study to compare alternatives of fuel oil and natural gas have been completed. Concurrent with the study, the DOE established a policy that directs the use of natural gas as an alternative to coal. This policy was reflected as a recommendation of the study.

An overall study of the HEF emergency cooling system and the primary water supply is underway. Bechtel prepared a draft analysis of the existing concept, including alternatives. Subsequent reviews and discussions have led to revisions in the overall water supply system(s) for primary and emergency cooling.

Preliminary floor plan layouts for the guardhouse (security center) and for the administration building have been prepared by Bechtel and are being reviewed by UCC-ND.

4.4.2 HEF process building

G. F. Kalb and J. N. Herndon

Significant progress has been made in developing the process building configuration that will be used as the basis for the HEF Conceptual Design Report. Preliminary floor plans, which will be issued for comment by October 1, 1979, will present the functional relationship and arrangement of major areas. The remaining details, such as meeting the exit requirements, locating toilet areas, and final room sizes, etc., will be completed during early FY 1980. The three remaining work tasks for the process building are dependent on the configuration and will be completed in early FY 1980. The cell ventilation study being prepared by Los Alamos Technical Associates (LATA) is on schedule; a draft report will be issued by October 1, 1979. The design criteria summary outlines have been completed and will be consolidated into final format by LATA during early FY 1980.

The building arrangement has been revised from that depicted in the October 1978 Interim Design Report. The general arrangement for the new concept can be seen in Fig. 4.3. The two storage pools and the krypton recovery cell have been moved to an area between the two main process cells. The number of building areas located within the tornado-hardened process building shell will be minimized. The main facility control center has been moved into a hardened area outside of the process building shell. These changes should result in improvements in function, cost, physical protection, and personnel exposure.

Fig. 4.3. The HEF process building plan at grade elevation. (Courtesy of Bechtel Corporation)

LATA is performing a scoping study on the load/unload system for the automated sampling system in the HEF (Sect. 4.3.5). The information obtained from this subcontract will be used to establish space requirements for the in-cell sample load/unload system and for maintenance.

4.4.3 General purpose cell systems

D. Macdonald and K. L. Walker

Two separate concept options are being developed by subcontractors (Sundstrand Energy Systems and Planning Research Corporation) for a floor-mounted manipulator system. This system provides remote manipulator coverage of all contiguous main cells and all process equipment modules. These studies not only will define the functional requirements of the system, but will provide for integration of other handling equipment, facility safety systems, and the transporter vehicle at the traffic control center. Both subcontractor studies indicate that full-volume coverage of the process equipment line can be achieved using the floor-mounted vehicle, thus adding viability to the center-aisle maintenance concept.

Sundstrand is also performing a study of methods to reduce process modules to scrap and to handle the scrap. Layouts of cutting devices, scrap handling, compacting, and packaging equipment were prepared to aid in establishing the scrap-cell configuration.

A schematic drawing of the transfer penetrations of the revised cell complex configuration has been completed. A maintenance flow diagram was developed to show equipment paths for both in-situ repair of the module and replacement of major process equipment assemblies. Contact maintenance facility layouts were revised to reflect the reduced dependence on the contact mode of equipment repair, and, in turn, the dependence on remote maintenance.

Work on the in-cell equipment placement drawings is continuing. These drawings are being updated and revised as the process and remote maintenance system concepts are developed. The cell complex and process building configurations to be included in the CDR will be established during October 1979.

4.4.4 HEF process systems

E. D. North, F. L. Peishel, and M. V. Keigan

The process systems design effort has progressed from a study of process options and preparation of material balance process flow diagrams to the sizing of process equipment and the arrangement of the equipment on process modules. The cell layout and the arrangement of modules in the cell, along with inter-module piping, are being developed. Floor sumps have been specified, and the piping to the rework system is being designed.

Module 562, the acid fractionator, has been selected for detailed design to permit the construction of a full-scale mockup module, which will be used to evaluate the capability for center-aisle maintenance. Bechtel has completed approximately 95% of this spatial verification model. Upon completion, the partial full-scale model will be sent to LASL for functional evaluation of the HEF process module spacing and remote handling requirements, utilizing LASL's electric master/slave manipulator. The model will contain simulated valve assemblies, pipe jumpers, flanges, and miscellaneous components typifying problem areas of a process module. The mockup will also be used to determine the optimum method of module location and of jumper design. A stiff jumper can tolerate lessened precision in module location.

A tritium fractionation system has been designed for use in the processing of thorium fuels. It is anticipated that voloxidation will be ineffective in releasing tritium from thorium fuels; consequently, the tritium will be released in the dissolver and remain with the recycle water system. The HEF design criteria for tritium containment requires that some means must be provided to concentrate the bulk of the HTO to a level that will permit disposal of tritium in an acceptable solidified waste. A volume of 59 gal/t of fuel processed has been arbitrarily selected for the waste stream in the concentrated product from the fractionator; this results in an HTO concentration of about 7 Ci/liter. The depleted product from the fractionator will be used to make up cold chemical solutions. A small amount may be further decontaminated and vaporized up the stack to maintain the plant water balance.

The characteristics of both Goodloe's and Sulzer's high-efficiency tower packings have been used in sizing the tritium fractionation towers. Both types of packings have been used in the production of heavy water (D_2O). A squared-off cascade using high-efficiency packing requires two columns of about 90 theoretical stages each, with about 50 ft of packing in each column. The first column is 8-ft in diameter, and the second is 5½-ft in diameter. The feed rate to the cascade is 300 liters/h. The tritium concentration in the fractionator streams is extremely low in moles per liter units, the reflux requirements are very large and about 180 theoretical stages will be required to make the separation.

The high reflux ratios in the columns result in large heat duties in the reboilers and condensers. Two options for supplying heat have been studied. The first option uses waste

heat from the high-level liquid waste storage tanks; the second makes use of vapor recompression on the overhead vapors to supply heat to the reboilers, thus eliminating the overhead condensers. The options are being reviewed to determine the one best suited to the HEF requirements.

4.4.5 Project support

B. F. Bottenfield, F. C. Davis, and D. P. Reid

Design criteria summaries for the major work breakdown structure elements have been completed. A contract was placed with the Los Alamos Technical Associates (LATA) to expand these criteria summaries into conceptual design criteria documents. This effort is scheduled to be completed in about six months; the criteria documents will then be forwarded to the DOE/ORO.

A quality assurance plan for the HEF conceptual design effort has been completed, approved by UCC-ND and the DOE/ORO, and issued. The plan is based upon the quality assurance requirements for a licensable facility as defined in 10 CFR 50 Appendix B.

5. TECHNICAL SUPPORT

O. O. Yarbrow

The various generic studies reported in this section are not specific to functional research and development areas but are important to the overall program. The particular areas being studied include facility operations, safeguards, nuclear engineering, the development of nonspecific process instrumentation and controls, and environmental assessment relative to the Hot Experimental Facility (HEF) design.

Ongoing activities of the Consolidated Fuel Reprocessing Program (CFRP) are summarized below; the details will be presented in topical reports.

5.1 Facility Operations

J. M. Chandler and D. E. Dunning

Facility Operations activities focused on facility modification and maintenance activities, energy conservation, and the preparation of program visual aid materials.

The 10-ft-diam equipment air lock connecting Building 7600 (Experimental Gas-Cooled Reactor containment) and Building 7602 was removed to provide storage space for some of the items for the Integrated Equipment Test (IET) facility that are awaiting installation in either the Integrated Process Demonstration or Remote Operations and Maintenance Demonstration.

In an effort to upgrade the mezzanine office area, the floors were tiled, and a split-unit-air-conditioning unit and sprinkler system were installed.

The roof plug on top of experimenter cell 2 was removed preparatory to the installation of fuel storage racks in the cell. A temporary roof cover was installed to cover the opening and provide shelter from the rain. The existing cell gravity drainage system was converted to a sump and pumped drainage system which will allow groundwater leakage to be directed to the storm sewer.

An existing stainless steel pan was placed in a room on the east end of Building 7604, and a dike was erected across the doorway to prevent any overflow into the room. This area is being used to store reagents and other supplies that require protection against cold weather. In addition, lighting and weatherproofing of the area was completed, and a roll-up door was installed in the east end of the building to provide access to the reagents stored there.

Building 7610 (formerly the fire-water valving house) is being refurbished for use as a storage area. Surplus pipe was removed, and holes were sealed to prevent water from entering the building. A 2-in.-thick concrete floor was poured to eliminate the wet floor problem which has, in the past, prevented the use of that building for storage.

The high bay area crane system has been isolated electrically and mechanically from the IET construction area. The M. M. Black Construction Company has started demolition work in the Remote Operational Maintenance Demonstration area.

Energy conservation work was continued, and there has been a permanent reduction of 54 kW in lighting. In addition, a total of 70 kW of installed lights are shut off at night, which leaves only 14 kW of lighting that burns continuously.

In continuing the effort to publicize the objectives of the program, a brochure on the Consolidated Fuel Reprocessing Program was prepared and distributed. A brochure describing the IET is being prepared, and a video tape describing the CFRP was completed.

5.2 Safeguards

H. T. Kerr

The safeguards task is developing the technology necessary to assure that effective domestic and international safeguards systems are incorporated into the design of the Hot Experimental Facility (HEF) and other reprocessing facilities. Many of our activities are generic in nature, whereas others are in direct support of the HEF design effort. The emphasis on international safeguards has been significantly increased by our participation in the International Atomic Energy Agency's (IAEA) International Working Group on Reprocessing Plant Safeguards (IWG-RPS) and by the activities associated with the Proliferation-Resistant Engineering Program. The rapidly increasing scope of safeguards activities has resulted in efforts to broaden relationships with other Department of Energy (DOE) funded safeguards groups [i.e., Los Alamos Scientific Laboratories (LASL), Sandia Laboratories, and Idaho Chemical Processing Plant (ICPP)] and with the Allied-General Nuclear Services (AGNS) staff.

5.2.1 Processing monitoring and accountability

Dynamic accounting instrumentation studies (R. E. Hurt and A. B. Crawford). One of the major premises of the safeguards task is that an effective dynamic accounting system would be a valuable safeguards component in future reprocessing facilities. There is considerable doubt, however, that the measurement instrument technology required to implement such a system will be available in the next few years. It is essential that instrumentation requirements be identified as precisely as possible in order to assess, as quickly as possible, the likelihood that the requisite instruments can be developed.

Using the HEF flowsheets as a reference, an initial estimate has been made of the instrument accuracies required to meet certain dynamic accounting objectives (specifically, the detection of a 2-kg loss of plutonium within 24 h with a 95% probability). Discussions with members of the Instrumentation and Controls task have indicated that one of the foremost problems is the measurement of fissile material concentrations in flowing streams. Work on the project paused at this point in anticipation of a joint effort with the LASL. The experience of the LASL staff with nondestructive assay instruments and the theory of dynamic accounting should permit this project to proceed at a faster pace.

Microscopic process monitoring (R. D. Hurt, A. B. Crawford, T. L. Hebble, and J. W. Wachter). The theoretical aspects of microscopic process monitoring (MPM) have been studied more closely, and it appears that the MPM strategy will be a productive one. Efforts are underway to apply MPM to part of the rotary dissolver support system in Building 7601 as an initial experiment. The purpose of the dissolver system experiment is to gain practical experience in implementing the MPM diversion detection logic on an operating process and interpreting its results.

A larger scale MPM experiment is being planned for the AGNS Barnwell Nuclear Fuel Plant. The second and third plutonium cycles at AGNS will be run with cold uranium, and the process control data will be recorded to serve as practice material for the MPM logic. It is anticipated that progress on the taped data will encourage other series of cold runs at AGNS to investigate the sensitivity of MPM.

Rotary dissolver dynamic balancing task (J. W. Wachter, J. A. McEvers, and R. M. Tate). A method of constructing real-time material balances utilizing process instrumentation is being demonstrated on the CFRP rotary dissolver. Information on process variables is accumulated by the Bristol VCS-3000 computer, converted to engineering units, and transmitted at 3-min intervals to the PDP-11/40 Component Development Data Acquisition System (CODEDACS). A computer code written for the CODEDACS computer calculates the current inventory in the instrumented feed and catch tanks and computes the material balance around the rotary dissolver on a continuous basis and as accumulated over a one-half hour interval.

A successful test of the dynamic balancing experiment was made during the Fe-5 experiment in which iron pellets and hulls were fed to the dissolver. Previous tests had not included solid feed. Two methods of calculating the total mass balance were studied, one primarily relying on changes in inventory and the other based primarily on flow rates.

Future efforts will also be directed toward improving the scheduling procedure which calls the balancing program into execution, improving the quality and reducing the quantity of line printer output, and devising more accurate algorithms for the mass fraction of $\text{U}/\text{HNO}_3/\text{H}_2\text{O}$ mixtures in the several tanks. A major task now being initiated is that of incorporating measurement uncertainties into the computation to attach error estimates to the calculated mass balance. Additionally, provisions for incorporating microscopic process monitoring are being included in the program.

Engineering safeguards program (W. J. Armento, W. D. Box, F. G. Kitts, A. M. Krichinsky, and J. A. McEvers). The principal objective of the Engineering Safeguards Program (ESP) is to demonstrate process monitoring as it might be accomplished by inspectors of a nuclear fuel recycle facility. Improved instrumentation and computer interfaces will initially permit the solvent extraction system operations, conducted in the Building 3019 Radiochemical Processing Pilot Plant, to be monitored as a volume balance.

Installation of the Building 3019 computer for process monitoring and safeguards is progressing well. The instrument/transmitter/computer connections have been completed and are being tested. Error analysis on the instrument readings is currently underway. As soon as these efforts have been completed, a static volume balance will be demonstrated. This will lead to a dynamic, near-real-time volume balance.

The in-line analyzer for uranium is being installed in a Building 3019 laboratory. The analyzer, which utilizes a cadmium-helium laser as the light source and fiber optics for light transmission, will be tested for linear response to uranium concentration. The analyzer concept will be examined for potential of plutonium measurement.

5.2.2 Hot Experimental Facility safeguards system design support

D. W. Swindle, Jr.

Criteria documents. The remaining three of the six safeguards system conceptual design criteria documents have been completed. These guidelines document the design considerations for the Intrusion Detection and Containment Surveillance System, the Material Control and Accounting System, and the Safeguards Response and Control System.

The criteria for the Material Control and Accounting System is undergoing final program review; the remaining two documents have been reviewed and are in use by facility designers.

International safeguards for the HEF. A report, written under subcontract with Science Applications, Inc. (SAI), to assess the impact of and the planning necessary for incorporating IAEA material accounting safeguards in the HEF, was completed on July 30. The report summarizes conclusions and special considerations that could impact the HEF's conceptual design (should it be designated a candidate facility for IAEA safeguards under the agreement between the United States and the IAEA). The study formulated a representative IAEA inspection plan by identifying what would be required of the facility in terms of operations and other facility requirements. The scope of SAI's work was limited to only material accountancy impact assessment and did not address containment and surveillance considerations.

Emergency evacuation system safeguards analysis. The assessment of emergency evacuation system concepts for the HEF was completed with the assistance of Sandia Laboratories. The evaluation identified alternatives for emergency evacuation from the HEF that would ensure that facility and nuclear materials were protected during emergencies. The study indicated that the HEF should be designed to comply with life-safety codes to the maximum extent possible, while remaining cognizant of safeguards concerns and requirements. The fundamental safeguards concept for emergency evacuation is that personnel in material access areas should be segregated from nonmaterial access area personnel during the evacuation process. Further results and conclusions are being documented.

Containment and surveillance system analysis for the Hot Experimental Facility (J. N. Cooley). The containment and surveillance system analysis for the HEF has proceeded to the point where draft documentation of the analysis is in progress. The analysis has identified those HEF cell-wall penetrations that would require monitors to provide indication of actual or attempts at material diversion. Recommendations have been formulated on possible sensor types applicable for containment and surveillance use. In addition, a sensitivity analysis is in progress to determine threshold amounts of special nuclear material that could be diverted without detection.

Hot Experimental Facility safeguards portal evaluation (F. M. Bustamante). Characterization of the safeguards equipment options for the HEF's entry-control portals was completed. This evaluation and characterization task involved the preparation of functional and procedural descriptions of the principal entry-control portals, the modeling of portal procedures and functions, and the assembling of plant personnel staffing estimates. The results of the evaluation have been transmitted to HEF designers.

Conversion of Sandia Laboratories Fault-Tree Drawing Code (F. M. Bustamante). The conversion of the Sandia Laboratories' Fault-Tree Drawing Code¹ from CDC System FORTRAN to IBM System FORTRAN has proceeded to the final stages of debugging. The code is being converted for use on Oak Ridge computers in order to assist in preparing fault-tree diagrams via computer graphics that could assist in safeguards system analyses. In addition, the code has application for use in reliability and safety analyses. A free-form data input subroutine package was added to facilitate data handling following the conversion of CDC FORTRAN parameters to IBM FORTRAN parameters. Test case runs have been initiated for identifying and expanding the code's graphic capabilities in reproducing fault-tree logic diagrams.

5.3 Nuclear Engineering

J. F. Mincey

Efforts this reporting period were concentrated into four broad areas. These include: the design of critical solution experiments, validation of neutronic codes against existing experimental data, criticality analyses of proposed HEF reprocessing hardware, and calculational support directed at predicting in-cell HEF radiation levels to assist in the development of remote handling equipment.

5.3.1 Design of U+Pu solution experiments

R. T. Primm III

The design of safe and economically attractive reprocessing equipment generally entails a trade-off between maximizing a plant's throughput rate against criticality-related considerations that tend to reduce throughput capacity. Without an adequate benchmark data base composed of experiments of sufficient quality and applicability to the equipment under design, subcritical conditions can only be ensured by resorting to extremely conservative limits (i.e., small vessels, low concentrations), which consequently tilt this trade-off towards uneconomical equipment designs and plant operations. Hence, an extensive set of critical benchmark experiments (~100) have been designed to provide criticality data to be used in the design of systems containing homogeneous blends of U+Pu.

At least three Pu/(U+Pu) ratios of 20, 40, and 60 wt % will be used (a small number of 30 wt % experiments are also planned). The concentrations to be used are 450, 400, 300, 200, and 100 g/liter concentrations of Pu+U. In addition, approximately 3 limiting concentration experiments (<100 g/liter U+Pu) are planned in spherical geometry. The previously mentioned upper concentration limit, 450 g/liter, was dictated by polymerization/precipitation considerations. The plutonium used will consist of two isotopic blends: 92 at. % ^{239}Pu + 8 at. % ^{240}Pu and 77 at. % ^{239}Pu + 23 at. % ^{240}Pu .

In addition to the spherical-geometry limiting-concentration experiments, three other geometries will be used. These consist of a variable thickness slab tank, an approximately 35.5-cm-diam cylinder, and an approximately 71-cm-diam cylinder. The slab and smaller diameter geometries will be used with concentrations ≥ 300 g/liter over the entire 20- to 60-wt % Pu/(U+Pu) range and for both isotopic plutonium blends. At least two reflectors, concrete and water, along with some bare experiments will be used with the small cylinder. These experiments provide data needed for the design of cylindrical equipment where geometry and concentration alone are relied upon in providing criticality control (i.e., pulse columns). Bare and water-reflected experiments will be conducted in the variable thickness slab tank in order to provide criticality data for designing U+Pu product storage tanks, sumps, and other such equipment for containing highly concentrated solutions in unpoisoned, high neutron leakage systems.

Experimentation with the variable thickness slab will also be conducted below 300 g/liter to provide needed data for the same type of HEF design applications. However, the approximately 71-cm-diam cylinder will be used in place of the smaller diameter cylinder at concentrations below 300 g/liter. Experiments in this vessel will generally be water-reflected, and in addition to the described unpoisoned set of experiments, will also involve comparable fissile solutions bearing gadolinium in concentrations ranging from about 2.5 to 0.3 g/liter.

Approach-to-critical calculations and detailed experiment flow charts have been completed. Fabrication of the required equipment will begin in early FY 1980.

5.3.2 Validation of neutronic codes

R. L. Pevy, R. T. Primm III, and J. F. Mincey

As described in earlier reports, an effort was initiated to procure standardized neutron cross-sectional processing and multigroup transport theory computer codes for predicting k_{eff} . The AMPX-II, KENO-IV, and CHERIE code systems, along with several cross-sectional sets, have been procured and copied onto a tamper-proof device such that any modifications to them must be approved by the Nuclear Engineering task.

Efforts are currently in progress using these codes to calculate all existing Fast Test Reactor (FTR) water-moderated fuel pin array data (generated by the CFRP and non-CFRP programs). This task is approximately 50% complete.

In addition, some existing FTR/fissile solution data have been calculated and are currently being analyzed as to whether their characterizing neutronic features (i.e., energy spectra) are sufficiently similar and inclusive enough to serve as a data base for fissile systems composed of dissolved and undissolved lumps of U+Pu oxide. Preliminary indications are that these data (for evaluating dissolver designs) are characterized by neutron energy spectra which are too well-thermalized and not sufficiently similar to spectra in HEF designs to serve as the sole data base. Hence, additional experimentation with more dissolver representative spectra may be needed to avoid excessive gadolinium concentrations which could significantly increase the volume of high-level waste produced by the HEF.

While calculating k_{eff} for previously reported critical FTR fuel pin arrays poisoned with metallic gadolinium pins, KENO-IV results indicated that multigroup gadolinium cross-sectional data (particularly for absorption) were in error. This particular type of error is notoriously difficult to detect because of the massive amount of cross-sectional data used in such calculations. In this instance, however, rather than dispersed through a solution as is the usual case, the gadolinium was physically separated from other materials. Because of a programming error, the particular version of the XLACS/AMPX code used to generate the multigroup cross sections from ENDF/B-4 did not treat resolved resonances for gadolinium below 3.05 eV. This resulted in the absorption cross section for the most thermalized group being too low by a factor of about 3000. Because the gadolinium was physically (and hence, mathematically) separated from other materials, nonabsorption probabilities greater than one were generated for the gadolinium pins by KENO-IV, using these erroneous cross sections. For systems where gadolinium is dispersed (as in HEF-typical solutions using gadolinium for criticality control), discrepancies between predicted and experimental values of k_{eff} would be (and possibly have been) observed from such an error. But because the gadolinium is generally homogeneously dispersed among other materials, the nonabsorption probability for such a solution would not seem unreasonable (i.e., not greater than 1), nor would the source of the k_{eff} discrepancy be difficult to detect.

5.3.3 Criticality evaluation of HEF Pu+U product storage module designs

J. F. Mincey

A series of detailed calculations was conducted using preliminary Pu+U product storage module designs. Two conclusions, based on neutronic considerations alone, were reached. The first is that a 60% less dense, concrete-like material, Borocast (distributed by Reactor Experiments, Inc.), is a significantly blacker neutron isolating material than borated concrete because of Borocast's larger boron content (5.6 wt % vs ~2 wt % for borated concrete). This additional blackness may result in smaller isolation thicknesses between slab

tanks than for borated concrete, allowing volumetric and mass reductions in the module designs. The second conclusion is that the stainless steel tank walls act as significant neutron reflectors decreasing allowable slab tank thicknesses. Thinner-walled tanks and alternate tank wall materials are being evaluated.

5.3.4 Radiation-level calculational support

E. J. Allen and J. V. Pace

The Nuclear Engineering Group initiated a computational effort during this reporting period to determine the in-cell radiation levels in the HEF. A program plan was formulated such that estimates of radiation levels would be provided on a useful and timely basis to the various tasks concerned with radiation damage in in-cell operating equipment. In addition, the Engineering Physics Division agreed to assist the Nuclear Engineering Group with the radiation level computational work. The radiation level calculational work can be divided into two areas: estimation of gamma-ray and neutron source strengths throughout the HEF, and development and verification of computational models for calculating the in-cell radiation levels.

During this reporting period, gamma-ray source levels for Prototype Large Breeder Reactor (PLBR) fuel have been calculated using the best available nuclear data with the ORNL Isotope Generation and Depletion Code (ORIGEN). Since PLBR fuel has a high burnup (150 MWd/kg) and a high specific power (0.15 MW/kg), the resulting radiation source strength is relatively high for nuclear fuel. Use of this radiation source strength for estimation of in-cell radiation levels is, therefore, conservative. In addition, computational methods have been identified for calculating, with reasonable accuracy, in-cell radiation levels. A computer program incorporating these methods is being written to calculate the gamma-ray dose rate at any position within the HEF.

5.4 Instrumentation and Control Systems

S. M. Babcock

This task will develop instrumentation systems and engineering techniques for the CFRP and provide basic instrumentation and control technology applicable to commercial plants. Instrumentation and control systems are required in support of laboratory experiments and in other highly specialized tests associated with the component- and process-development tasks of the CFRP.

5.4.1 Sensor development

M. L. Bauer, D. T. Bostick, J. T. Delorenzo, D. D. McCue, D. W. McDonald, H. H. Ross, J. E. Strain, and W. L. Zabriskie

The evaluation of the electrochemical monitor in the system for flowsheet studies in Building 3508 is now complete. Several problems were encountered that did not appear in the bench testing of quiescent solutions. The following conclusions were reached regarding the utility of an electrochemical monitor as a remote sensor: (1) in a mixed hydroxylamine nitrate (HAN)-hydrazine nitrate (HYN) solution, a platinum working electrode can be used to detect the presence or absence of HAN-HYN; (2) quantitative measurement of either reductant in the mixture is not practical; (3) the acidity of the stream can be estimated from the potential difference between H_2 and O_2 generation; (4) the glassy carbon working electrode can be used to estimate the concentration of plutonium and the approximate

ratios of Pu(III):Pu(IV) if the ratio ≥ 10 or ≤ 0.1 ; and (5) the glass carbon electrode is subject to fouling and loss of sensitivity. Sensitivity is restored by mechanical cleaning and polishing. A report which details the investigation of electrochemical sensors and the conclusions reached is now in preparation.

A commercial spectrophotometer equipped with a flow cell was used to determine the uranium concentration in aqueous streams of the Building 3508 system. The results obtained from the multi-wavelength photometric procedure agree within 5% of those obtained from laboratory analyses of collected stream samples. The accuracy of the photometric method was considerably better than that of a digital densitometer, which also monitored uranium concentration in the same process lines. Plutonium has subsequently been added into the Building 3508 system lines. A mini-spectrophotometer is being acquired which will be placed in the sealed glove boxes for in-line U-Pu analysis. The mini-spectrophotometer is being calibrated at present. A potentiometric procedure is being developed for the determination of HNO_3 in 30% tributyl phosphate (TBP). The standards will be used to develop a photometric procedure for determining uranium in organic streams.

The in-cell portion of the neutron poison monitor has been released for fabrication. The design includes remote maintenance features and with minor radiation hardening, will be suitable for HEF exposure. A 100-ft-long special Twinax cable, suitable for radiation exposure and high (140°C) temperature was procured and tested in conjunction with a ^{10}B -lined proportional counter. The balance of the 100-ft cable was quite good at 30 dB. Three amplifiers were tested, an ORNL instrumentation amplifier, a Burr-Brown model 3622, and Canberra model 960D charge-sensitive amplifier. The Burr-Brown amplifier seemed to have the greatest bandwidth. Although this amplifier displayed the greatest electronic noise, counting efficiency was not affected.

Further tests have been conducted on the lab model of the free acid monitor in the range from 0.038 M to 11.77 M HNO_3 . The sensitivity at the low end was acceptable but demonstrated positive transients that were traced to aerosols that had inadvertently gotten into the vapor path. The mechanical design of the instrument will eliminate this problem. At the upper end of the molarity scale (10.5 M), the results were double valued. The lowering of the operating temperatures of the lab model returned the results to reliable single valued measurements but with an untenable increase in instrument response time. Several schemes to operate at lower temperatures while still retaining suitable response time have been investigated. The choice and commitment for the prototype is imminent. The total package design is to contain an optional choice of condenser depending upon the environmental conditions of installation. The first is a Hilsch tube, driven by plant air for higher radiation exposure areas, and the second is a thermoelectric cooler for medium to low radiation areas.

One of the serious problem areas in the development of the uranium monitor has been the identification of a supplier of long quartz fiber optical bundles. This appears to have been solved by the recent entry of an American company into the field. Components are on order. A stainless steel in-cell module is presently being fabricated and will contain plano/convex lenses that enhance signal transmission tenfold. Eventually, spherical surfaces will be ground directly on the end of the sapphire window that interfaces with the process fluid to accomplish an equivalent result.

Physical sensor development. The DuPont ultrasonic flowmeter has been modified by replacing the sensor tees and sensor tube with Swagelok tees and a 1/2-in.-diam tube which was twice the length of the original. This was done to increase the path length and, hence, the frequency shifts at low flows. Unfortunately, it also increased the attenuation, and the

original electronics do not have sufficient sensitivity to pick up the weaker signal. Further tests will be made when the laboratory electronic modules, which are on order, have been received.

A Controlotron clamp-on ultrasonic flowmeter was received and installed in the flow calibration loop. Initial tests showed that the analog output of the meter reflects a precision in the measured flow rate better than 5% at 50 liters/h. This is substantially better than the DuPont meter, which had uncertainties of more than 100% of reading in this flow range.

A thermal mass flowmeter was ordered. The manufacturer claims 1% accuracy, 100:1 rangeability, and a minimum detectable flow rate of 1 g/min.

A liquid level test stand, which consists of two 8-ft-high by 12-in.diam columns, was fabricated for use in evaluating level sensors. Liquids can be pumped from one column to the other with the discharge either into the bottom or top of the receiving vessel. One of the columns can be air-sparged. The valving is solenoid-operated so that the test rig can be easily put under automatic operation.

Larry Lynnworth of Panametrics, Waltham, Massachusetts, brought two ultrasonic torsion wave level and density sensors to ORNL for demonstration. These sensors appear to be very promising for both level and density measurements. The sensor itself is a flat stainless steel ribbon, 1 x 2-mm-wide which is suspended in the tank. The sender-receiver is simply a solenoid coil into which is inserted a magnetostrictive rod attached to the end of the flat ribbon sensor. Reflections are produced at the liquid-gas interface. Detection of a liquid-liquid interface has not yet been tried. The sensor can be zoned to provide a density profile of the tank, which would be valuable in detecting stratification.

5.4.2 Special measurements

G. L. Ragan, C. W. Ricker, G. G. Slaughter, E. D. Blakeman, M. M. Chiles, and D. T. Ingersoll

Spent fuel assay. The objective of this subtask is the development of a nondestructive assay system for the determination of the total fissile content of spent fuel and blanket subassemblies at the head-end of a reprocessing plant. Having successfully completed a proof-of-principle (POP) experiment in FY 1978, the efforts during FY 1979 have been on (1) the investigation of methods to measure the isotopic compositions of the fuel in the subassemblies; (2) the demonstration of the POP assay system using irradiated fuel subassemblies rather than simulated radiations as was used in the POP experiments; and (3) the performance of follow-on POP experiments to better characterize, and hence, to more completely specify the design parameters for the head-end assay system.

Calculations have been used to extend the experimental results obtained in the POP experiments. To validate the calculational method, several experimental situations have been simulated and the calculated and measured results have been compared. A comparison of measured and calculated assay sensitivities as a function of axial position within our test subassembly is shown in Fig. 5.1. Both sets of data are normalized to unity at axial position $Z=0$. The axial extent (full width at half maximum) of the sensitive region is 24 cm. A comparison similar to radial sensitivity gave an edge-to-center ratio (averaged over axial length) of 1.127 (calculated) vs 1.140 (measured). The above comparisons tend to confirm the validity of the calculational model and method.

The above calculational method has been used to study isotopic sensitivity effects and ways that isotopic composition can be determined. Relative assay sensitivities for seven common heavy-metal nuclides were determined by isotopic activity calculations for the fuel-zone neutron spectra for three different fuel compositions. The results, expressed as relative

ORNL-DWG 79-14557

Fig. 5.1. A comparison of calculated and measured axial sensitivity for 7.1% enriched fuel and 450–650 keV pulse detection.

total fission-neutron production (relative to ^{239}Pu taken as 100), were essentially independent of the subassembly fuel and were as follows: ^{232}Th , 0.1; ^{233}U , 170; ^{235}U , 110; ^{238}U , 0.7; ^{239}Pu , 100; ^{240}Pu , 7.7; and ^{241}Pu , 140. Thus, the system has comparable sensitivities for the various fissile nuclides and shows good discrimination against fertile nuclides. These results indicate that an approximately 1.7-fold range of fissile-nuclide assay sensitivities is to be expected in assaying various fuels. They also can be used to determine the uncertainty in total-fissile assay results corresponding to a given uncertainty in relative isotopic composition. This calculated 1.7-fold range of fissile-nuclide sensitivities, based on total-neutron detection, is found to be only about half as large as that for a similar system based on delayed-neutron detection because of the wide variation in delayed-neutron fraction among fissile nuclides.

Several methods of determining isotopic compositions have been investigated. A relatively simple, yet promising, method is based on measuring the ratio of the signal for alternative sample-surrounding filters relative to that for the reference 3-mm ^{10}B filter.

The demonstration of the POP assay system using spent fuel is awaiting the availability of suitable fuel, which is expected during the next fiscal year. Plans call for assaying Browns Ferry fuel after it has been chopped into short pieces and placed in cans containing 2 kg of fuel each. Four cans will be stacked in a canister to simulate a fuel subassembly and assayed by performing an axial scan of the 8 kg of fuel in the canister. After this nondestructive assay, the fuel will be destructively assayed at the Transuranium Processing Facility, thus providing a comparison of the two types of assay.

Leached hulls assay. The objective of this subtask is to design a proof-of-principle experiment based on the nondestructive assay method considered testable to meet the performance specifications and safeguards criteria when applied to the design of a leached hulls monitor for the HEF. An active neutron interrogation assay method similar to that used in the head-end POP experimental system has been selected as the method to be used for the POP of the leached hulls monitor.

Experiments preliminary to the design of the leached hulls monitor POP apparatus were conducted in cell B of the Thorium-Uranium Recycle Facility, using Sb and Cf sources placed by a remote manipulator. The POP monitor utilizes a hydrogenous filter to differentially attenuate low-energy interrogation neutrons and high-energy response neutrons, following a design by Filss.² Attenuation curves were taken for plain water and water borated to 0.4 M boric acid (the maximum possible at room temperature). Signal-to-background ratios for a 500-mg sample of ²³⁵U were obtained as a function of source and sample height above the bottom of the tank. The best signal-to-background ratio was obtained with the source at 6 in. and the sample at 5 in. above the bottom of the tank. Detector moderator optimization measurements indicated that 1 in. of moderator above the counters and 3 in. below gave the highest counting rate for simulated response neutrons through 6 in. of filter.

5.4.3 Mechanical surveillance

The prototype dissolver vibration monitor was tested during a recent 32-h run. A considerable amount of data from the monitor was either recorded or logged during this time. From this baseline data, the effects of normal operating parameters (i.e., flapper valves, acid and water flows, etc.) will be evaluated, the suitability and effectiveness of the signals for monitoring both for mechanical anomalies and material movement will be evaluated, and preliminary warning and alarm settings for signals during this kind of operation will be made. The monitor worked without any significant problems throughout the test. However, it became apparent that, in order to have a useful monitor, automatic continuous logging of each signal instead of the regular, but infrequent, manual data logging would have to be included.

The presently installed vibration monitor is capable of calculating the root-mean-square (rms) vibration level of only one channel. The usefulness of the vibration monitor to the dissolver operators could be greatly increased by expanding the system to provide a continuous rms vibration level indication and recording for all 14 channels.

5.5 Environment and Safety

M. B. Sears

The environment and safety task includes the activities related to site selection and the preparation of the environmental impact statement (EIS), the preliminary safety analysis report (PSAR), and the final safety analysis report (FSAR) for the proposed HEF. A long lead time is required in the site selection process to allow time for the detailed characterization needed in order to ensure that the site meets the engineering requirements and is acceptable from a public health and environmental viewpoint, and to allow time for the preparation of the EIS and PSAR documents before the start of construction. As an example, two years of meteorological data at the plant site are required for the PSAR calculations.

The criteria for evaluating potential sites are being developed, and a draft report for internal review is almost complete. Exxon Nuclear Company, Inc., Richland, Washington, through a small subcontract, is providing assistance in developing schedules and manpower requirements, as well as technical consultation.

The Savannah River Laboratory (SRL), under contract to the CFRP, is reviewing the HEF flowsheets and concepts to identify potential safety-related incidents, their causes, consequences, and to recommend safety features. For the purpose of this review, the HEF process is divided into study groups. The final draft report of one group, covering all operations through feed adjustment, has been approved for issue. Process equipment, including that to be used in the solvent extraction systems, is also being evaluated.

References

1. D. A. Oliver, *Fault-Tree Drawing Program User's Instructions*, SLA-73-0409, Sandia Laboratories, April 1973.
2. H. P. Filss, "Direct Determination of the Total Fissile Content in Irradiated Fuel Elements, Waste Containers, and Other Samples of the Nuclear Fuel Cycle," *J. Nucl. Mater. Manage.* 8(2), 74(1979).

6. HTGR FUEL REPROCESSING

B. L. Vondra

This section presents a summary of process R&D work performed at General Atomic Company and at Oak Ridge National Laboratory on the reprocessing of HTGR and GCFR fuels.

6.1 Studies and Analyses

H. C. Carney, General Atomic Company

The objectives of this task are to (1) define unique reprocessing development and facility requirements for spent GCFR fuel, compared with present LMFBR reprocessing plans and facility designs; (2) evaluate the impact of HTGR fuel design changes on reprocessing requirements and costs; (3) confirm flowsheet requirements and prepare material balances as required for HTGR reprocessing and waste streams; and (4) assess HTGR fuel reprocessing head-end alternatives.

6.1.1 Evaluation of GCFR fuel reprocessing

V. H. Pierce

The initial milestone report completed in the previous quarter identified GCFR core and fuel design features that would impact the Hot Experimental Facility (HEF) reprocessing flowsheets. The principal items and their impact are listed in Table 6.1.

These findings, along with current information on the HEF conceptual design progress, were reviewed this quarter. From the standpoint of the GCFR spent fuel reprocessing assessment, two HEF conceptual design developments were noted:

1. The solvent extraction system is being revised to a high-decontamination Purex-type flowsheet with a uranium-plutonium coprocessed product. Thorium base fuel would be processed on a campaign basis as an added flowsheet capability.
2. Advanced head-end disassembly and shearing systems requirements and design have been developed and are being prepared for prototype design bid. These systems are to be incorporated into the HEF conceptual design.

HEF process flow diagrams (PFD's) from the October 1978 Interim Design Report were reviewed to define GCFR spent fuel reprocessing PFD development requirements. Process and mechanical handling system functional description writeups and PFD revisions covering GCFR cask unloading, fuel assembly handling, and fuel assembly pool storage are being prepared. Process conceptualization has been initiated for handling the GCFR charcoal fission product traps as a radioactive waste material.

**Table 6.1. Impact of GCFR core and fuel design features
on HEF flowsheets**

Source	Impact
Fuel Cycle	
<ul style="list-style-type: none"> ● Plutonium-uranium core and blanket ● NASAP* proliferation-resistant cycles using plutonium-uranium core with thorium radial and/or axial blankets 	<ul style="list-style-type: none"> ● None, same as LMFBR base technology ● Added process to remove tritium from thorium blanket pellets ● Thorex solvent extraction processing ● Thorium and denatured ^{233}U product handling and storage ● Head-end disassembly and shearing equipment to separate thorium axial blanket pellets
Mechanical design	
<ul style="list-style-type: none"> ● Helium reactor coolant ● Fuel assembly and rod dimensions ● Assembly and core fuel rod charcoal fission product traps 	<ul style="list-style-type: none"> ● No sodium removal operations from fuel assemblies ● No sodium waste handling ● Mechanical handling and head-end process equipment capable of handling a range of assembly and rod sizes ● Head-end disassembly and shearing equipment capable of separating traps from hardware and fuel parts ● Process to handle traps as waste

*Nonproliferation Alternative Systems Assessment Program.

6.1.2 HTGR recycle plant data base N. D. Holder and B. B. Haldy

A supplemental report was prepared to document changes in the commercial recycle plant design occurring since the original conceptual design in 1974–75.¹ The major changes include (1) high-gain, high-enriched fuel design (the change to medium-enriched fuel was not covered in the scope of this task); (2) solidification of thorium product; (3) vitrification of high-level liquid waste and retired particles and hulls; (4) fixation of ^{14}C as CaCO_3 ; and (5) addition of a cold fit-up facility to improve maintenance capabilities. Several minor changes are also documented, as well as a list of pending design changes not included in this

update. The resulting direct construction cost estimates, equipment lists, and space requirements from the update are included in the report. The data from the update were used as input to Alternate Fuel Cycle Evaluation Program studies being performed under another DOE contract.

The direct construction cost estimate associated with the Target Recycle Plant is stored on a computerized data base. A user's manual for the data base has been drafted and is being published.

The manual describes capital cost handling for the plant and reports that a data storage and retrieval system has been designed to allow continuity in cost estimating and control from conceptual recycle plant design through construction. Facility capital costs are stored, and the data can be retrieved in several ways to provide (1) information for cash flow analysis to determine recycle contribution to fuel cycle economics, and (2) selected information for engineering cost/benefit studies. While the manual addresses a recycle plant, the data storage and retrieval system is generic and can be used to handle capital costs for any type of manufacturing facility.

6.1.3 Flowsheet and material balance

N. D. Holder and B. B. Haldy

Characteristics for MEU (medium-enriched uranium) spent (both initial and makeup) HTGR fuel elements and HEU (high-enriched uranium) spent recycle fuel elements have been defined;² reprocessing flowsheets and material balances also were developed.³ Based on the waste streams identified in the reprocessing material balance, waste treatment flowsheets and material balances are being defined. A simplified summary of the flowsheets is shown in Fig. 6.1. Material balances have been completed and are being reviewed.

6.1.4 HTGR fuel reprocessing head-end alternatives

D. M. Bender, V. H. Pierce, J. S. Rode, N. D. Holder, and L. Abraham

The objective of this task for FY 1979 was to identify and make an initial technical assessment of ways to reduce the amount of solid carbonate waste resulting from HTGR spent fuel reprocessing. The present reprocessing head-end flowsheet reduces fuel element graphite moderator and graphite matrix materials by burning.

The gaseous CO₂ waste is solidified as calcium carbonate by chemical treatment with slaked lime. Carbon-14 and other small quantities of radioactive products are contained in this carbonate waste.

Over 20 alternate head-end unit operations and three alternate fuel element designs have been studied in various degrees since the mid 1960's. Several groups have considered the alternatives, including General Atomic, ORNL, the Federal Republic of Germany, and Japan's Atomic Energy Research Institute.

Of the work identified by this initial effort, the following conclusions were drawn with regard to the current objective of reducing the volume of solid carbonate waste:

1. Of the many methods studied for mechanical, chemical, and electrical debonding for separating fuel-free graphite from the fuel-bearing material, sawing and/or pressing are identified as having some potential, based on the results of initial feasibility work. The other methods have been shown to be impractical, overly complex, or to result in unfavorable chemical or physical environments.

Fig. 6.1. HTGR reprocessing waste treatment. (Courtesy General Atomic Company)

2. All of the alternate fuel designs studied to date allow separation of the fuel-bearing material from the bulk of the fuel element graphite.
3. Alternate combustion processes and burner initial off-gas treatment processes were identified as having future potential. Included are (1) the JAERI studies into the combustion of graphite in a CO₂ atmosphere (the burner off-gas is decomposed to yield solid carbon for waste disposal and CO₂ for recycle to the burner); and (2) the FRG concept to react burner off-gas particulates to form methane, which is subsequently decomposed into carbon for disposal and hydrogen for recycle to the burner off-gas system.
4. A number of combinations of alternate processes with current unit operations can be conceptualized to result in a head-end flowsheet with the technical potential to reduce the volume of solid carbon-containing waste.

The technical evaluation of potential alternatives is continuing, and follow-on assessment recommendations will be made.

6.2 Head-End Studies

W. S. Rickman, General Atomic Company

6.2.1 United States-Federal Republic of Germany Cooperative Program

W. S. Rickman and J. S. Strand

This program coordinates development work on graphite-based nuclear fuel reprocessing in the United States and the Federal Republic of Germany. Project work statements in 14 different areas of development facilitate the transfer of fuel reprocessing technology on a formal basis. Jointly prepared program plans are used in the most active areas of exchange to further define the scope and timing of cooperative efforts.

A Joint Prototype Head-End Facility (JPHF) is in the early stages of conceptual design. This will be a cold, remotely maintainable, full-size facility. It will be cooperatively designed, built, and operated using both U.S. and FRG reference fuel types.

A program plan is being written for a joint fuel processing demonstration (JFPD), in which nonirradiated FRG fuel (spherical elements) will be processed through the General Atomic HTGR Fuel Reprocessing Pilot Plant. This will be an important verification of design concepts currently being incorporated in the JPHF. Commonality of reprocessing equipment for both spherical and prismatic fuel elements is one of the major goals of the cooperative program. The total quantity of fuel elements to be processed will exceed a metric ton. This will provide adequate equipment operating time to ensure the validity of the results.

6.2.2 Crushed fuel element burning

J. M. McNair and D. E. Fields

The major objective in the crushed fuel element burn subtask is to define and develop the control systems to automate the primary burning process. The 0.20-m primary burner was selected as the system to be used to develop the control schemes needed to automate the primary burning process. The burning process was divided into three distinct regimes for process control: (1) startup, (2) steady-state, and (3) shutdown (tailburn). Significant progress has been made in automating two of these regimes: startup and steady-state.

The steady-state regime was selected as the first portion of the burner operation to be developed. The major variables to be controlled during steady-state operation are bed temperature, fluidization velocity, and burn rate (both fines and main bed). Several secondary variables must also be controlled for safety and process considerations.

The control algorithms were developed, and the programming of both the supervisory and process control computers was completed. Several burner runs were made to test the control schemes. After some minor modifications and tuning of control loops, steady-state operation at the desired burn rate [200 g/min with fines burning and at a steady bed temperature (925°C)] could be maintained with less than a 1% variation in process variables.

The next step in the study was to automate the startup sequence. Control systems were developed to initiate fluidization flow, heat the burner, ensure bed mixing during heatup, initiate fines recycle, start and gradually increase oxygen flow until the desired burn rate is attained, initiate cooling air flow, begin fines burning, and provide a smooth transition between the startup and steady-state regimes. Many burner runs were made to develop and tune these control systems.

The final step in the automation process, that is, the development of the control schemes for the shutdown (tailburn) regime of operation, will be completed by September 30, 1979.

Several burner modifications have been made to assist in the automation. Valve positioners have been added to the gas flow control valves. Logic function channels have been added to the process control computer. The flow transmitters were calibrated and adjusted to remove signal oscillations. Circuitry was added to ensure that at zero flow, the computer received a zero signal so that burn-rate calculations would be more accurate.

6.2.3 Particle classification, crushing, and crushed-particle burning

J. B. Strand

Air classification. The design of advanced fuel types will affect the efficiency of separation of fissile and fertile particles by air classification in proportion to the differences in the densities and diameters of the particles. Parametric studies on current fuel particles were completed earlier. Fuel particles designed for a middle-enrichment uranium fuel cycle are being produced for classification tests. The fertile particles (TRISO coated ThO₂) have been received. Fabrication of the fissile particles (TRISO coated UO₂) is underway.

The separation of fissile and fertile particles produced by the Federal Republic of Germany will also be studied using General Atomic's air classification system. Test plans for the classification studies were approved, and the particles were received. The terminal velocities of the fissile (TRISO coated UO₂) and fertile (TRISO coated ThO₂) fuel particles were separately determined in a series of tests. Using these data, a series of tests using blends of particles was completed to study the separability of the particles. Analytical results from these tests are pending.

Secondary (crushed fuel particle) burning. The initial gas distributor in the 0.10-m secondary burner has been replaced by a remotely removable distributor. In addition to the remote features, the flange connection is located outside of the high-temperature zone. The initial testing of the new distributor was completed with no operating problems. Observation of the distributor will be an ongoing task in conjunction with use of the burner for further process data.

With the present design of the secondary burner's filter chamber, the in-vessel filters are difficult to replace remotely. A new design which eliminates the problem and replaces the side feed charging port with a top port has been completed.

The design evaluation of the secondary burner⁴ concluded with a recommendation that the burner tube, susceptor, heating coils, and cooling shroud be a unitized (i.e., integral) construction for remote removal and replacement. A burner with this feature has been designed.

6.2.4 Dry solids handling

C. J. Everline, N. D. Holder, J. M. McNair, and W. S. Rickman

Pneumatic transport component test loop. The component test loop is being used to determine wear in pipe bends and failure rates of typical solids transport equipment. The test loop operated successfully for 3900 out of 4000 cycles, transporting crushed graphite. The failures typically involved material holdup problems associated with degradation to a fine powder. Since the same material is continuously recycled, this cannot be considered typical of plant operation. After 275 h of operation with graphite, the test material was replaced with a mixture of crushed graphite and BISO- and TRISO-coated fuel particles typical of a large HTGR spent fuel element. The rig has been operated for an additional 900 cycles and 90 h using the fuel element mix. The cycle time was about 30% longer, blower power was increased 30%, and a vibrator was added to clear the material from the lower bunker. The vibrator operation has been erratic, and a new one has been ordered. Thirty failures during the 900 cycles are principally associated with vibrator failure. Pipe bend wear rates with pure graphite were negligible; bends are not yet due to be checked with the fuel element mix material.

Remote coupling devices. A selection of remote and nonremote coupling devices was purchased or borrowed to evaluate their applicability to HTGR reprocessing dry solids handling and their suitability for remote maintenance activities. After a general evaluation to eliminate those that might cause particle breakage and/or material holdup problems, the remaining couplers were tested at the cold manipulator station at the GA hot cell for ease of handling. The Unibolt breech lock connector was very easy to handle with only simple changes for manipulator handling. However, it is too large and heavy for the desired application and would have to be fabricated to lighter specifications. The G&H fast clamp was also easy to handle but is too light for hot-cell operation. A similar design of sturdier proportions is being fabricated by Rocky Mountain Nuclear Engineering. Both couplers will require seal redesign to optimize their application to HTGR fuel particle handling requirements. The Rocky Mountain Nuclear order includes an improved seal design.

Sampling plan and sampler criteria. This task was completed with the development and publication of a sampling plan and generic sampler criteria.⁵ In general, nuclear safety and accountability requirements for HTGR dry head-end reprocessing will not require process stream sampling. Sampling will usually be required only to monitor process performance.

High-temperature rotary feed valve. Design and fabrication of a high-temperature rotary feed valve is complete. At temperatures up to 700°C (1300°F), the alloy construction allows continuous metering of abrasive particulates into a fluidized-bed combustor. The valve design minimizes the possibility of leakage through the valve as well as to the environment.

The components of the high-temperature rotary valve are shown in Fig. 6.2. Some of the outstanding features include wear coatings; solid-film-lubricated, self-aligning bearings;

Fig. 6.2. High-temperature rotary valve feeder continuously meters high-temperature abrasive particulates into a fluidized-bed combustor. (Courtesy General Atomic Company)

and a hollow drive shaft to discourage heat transfer to the bearings. To prevent solids leakage, buffer gas, graphite filament packing, and stainless steel bellows are used.

The rotary valve has been mounted on a test bench. Since gas and solids leakage through the valve affects the efficiency of operation, a series of cold shakedown runs is underway to determine the actual leakage rates at various operation conditions. Testing will continue for several months.

After verification of satisfactory solids handling capabilities, the new rotary feed valve will replace the existing one on the 0.40-m primary burner.

6.3 Hot Laboratory Head-End Studies

V. C. A. Vaughen, ORNL

6.3.1 Hot laboratory development

C. L. Fitzgerald and O. L. Kirkland

The final results of the studies with the FTE-16 fuel have been incorporated into a report for publication as ORNL/TM-7030. The fuel test element FTE-16 was irradiated in the Peach Bottom reactor for 512 effective full power days (EFPD). The fuel particles were the Fort St. Vrain type, TRISO-coated $\text{Th}_{2.75}\text{UC}_2$ fissile, and TRISO-coated ThC_2 fertile. Two samples of fuel were processed through the head-end flowsheet. The steps in this flowsheet are: (1) fuel crushing, (2) primary burning, (3) sieving to separate fertile and fissile particles, (4) crushing of each fraction (separately), (5) secondary burning of each fraction, and (6) dissolution of each fraction.

In each experiment, the fuel rods were selected, crushed, and burned in the primary burner. (The first experiment was designated F-16-1-6 and the second F-16-1-7.) Burner operating conditions were 850 to 875°C in 5% O_2 –95% N_2 with a fluidizing velocity of 0.82 m/s for the first experiment and 0.88 m/s for the second. The burner products were weighed, separated into fertile, fissile, and fines (broken particles) fractions. The fertile and fissile fractions were crushed in the roll crusher, weighed, and burned in the secondary burner at 850 to 875°C. Operating conditions were 0.76 m/s fluidizing velocity with 20% O_2 –80% N_2 . The burner products were weighed and dissolved to 250 g/liter (U+Th) in Thorex reagent for 12 h at reflux.

Overall, very good agreement was obtained between the calculated and predicted weights and the experimentally measured values. Similar good agreement was attained for the solution and gas sample compositions; however, the analysis of the solid samples did not yield consistent enough values to be useful in the run analysis. Several points of interest did come from these studies. In the first place, there seemed to be preferential breakage of the fissile particles over the fertile particles, perhaps by a ratio of about 5 or 10-to-1, based on calculations using the isotopic compositions of the fines product. There was a failure to break all the fissile particles before the second of the broken fissile particle burning runs, perhaps due to a shifting of the gap in the particle crusher. Finally, severe crossover was experienced, although the cause for this effect was not established.

The sintered metal filters were removed from the secondary burner and analyzed non-destructively by gamma-scanning after about 8 h of use. Approximately 1.5% of the cesium inventory was found on these filters; no pressure drop problems were experienced.

6.3.2 Long-term fission product volatility

C. L. Fitzgerald and O. L. Kirkland

The long-term fission product volatility experiment has been in progress for about three months at 875°C. Analytical measurements after the second one-month period indicate that the semivolatile fission products have accumulated on condenser surfaces maintained at about 400 to 500°C during the test. The total inventories on the condenser coil at the conclusion of this period were about 47 mCi ^{106}Ru , 36 μCi ^{125}Sb , 1.4 mCi ^{134}Cs , and 4.5 mCi ^{137}Cs . These values compare with about 2.1 mCi ^{106}Ru and traces of the others found after the first month.

6.3.3 Processing of high-level HTGR-specific solid wastes

K. H. Lin, W. B. Howerton, C. L. Fitzgerald, and O. L. Kirkland

Leaching experiments continued for the hot SiC-matrix cylindrical pellets. Table 6.2 shows the average leach rates for ^{125}Sb , ^{134}Cs , ^{137}Cs , and ^{154}Eu , calculated from the experimental data after leaching periods of 43, 77, and 112 d. As illustrated, reduction in the leach rates of selected radionuclides is observed for all samples when the leaching period was extended from 43 to 77 d. The decrease in the rates for ^{134}Cs and ^{137}Cs was nearly an order of magnitude. Insignificant changes in the leach rates for all nuclides (except for ^{154}Eu) were noted for the period between 77 and 112 d of leaching. Sample II (50% clay–50% SiC hulls; 1000°C sintering temperature) again displayed the lowest leach rates of cesium isotopes.

Table 6.2. Leaching behavior of immobilized radioactive SiC hulls^a

Sample ^b	Clay-Glass SiC hulls composition (wt %)	Leach time (d)	Average leach rate (fraction·cm/d) ^c			
			^{125}Sb	^{134}Cs	^{137}Cs	^{154}Eu
I	50-0-50 (fissile)	43		4.4(–4)	3.8(–4)	
		77	2.2(–6)	9(–5)	6.8(–5)	
		112	3.3(–6)	8.2(–5)	6.2(–5)	1.2(–6)
II	50-0-50 (fissile)	43	1.8(–6)	2.9(–5)	2.5(–5)	3.6(–6)
		77		8.8(–6)	7.4(–6)	6.2(–7)
		112		7.6(–6)	7.6(–6)	
III	25-25-50 (fissile)	43	1.0(–5)	1.4(–4)	1.2(–4)	
		77	7.0(–6)	4.2(–5)	3.1(–5)	
		112	6.3(–6)	4.6(–5)	3.4(–5)	
IV	25-25-50 (fertile)	43	2.0(–4)	4.3(–5)	5.7(–5)	6(–7)
		77	1.2(–4)	1.3(–5)	1.5(–5)	
		112	6.5(–5)	1.1(–5)	1.6(–5)	

^aFrom FTE-16 TRISO-TRISO fuel particles.

^bSintering temperature: 1000°C for II and 800°C for all others.

^cAverage values for two duplicate samples. The number in the parentheses represents the power of ten.

References

1. *Conceptual Design Summary and Design Qualifications for HTGR Target Recycle Plant*, ERDA report GA-A13365, General Atomic Company (April 30, 1975).
2. G. D. Zane, L. Georghion, and C. J. Everline, *Large High-Temperature Gas-Cooled Reactor Medium-Enriched Uranium Spent Fuel Element Definitions and Block Flows*, DOE report GA-A14980, Vols. 1 and 2, General Atomic Company (August 1978).
3. L. Abraham, *Reprocessing Flowsheet and Material Balance for MEU Spent Fuel*, DOE report GA-A15145, General Atomic Company (October 1978).
4. J. S. Rode, *A Design Evaluation of the 20-cm (8-in.) Secondary Burner System*, ERDA report GA-A14510, General Atomic Company (August 1977).
5. C. J. Everline and N. D. Holder, *Sampling Plan and Sampler Criteria for the Dry Head-End System in a Commercial High-Temperature Gas-Cooled Reactor Fuel Reprocessing Facility*, DOE report GA-A15566, General Atomic Company (August 1979).

7. PYROCHEMICAL AND DRY PROCESSING METHODS

C. H. Bean and M. J. Steindler (Argonne National Laboratory)

Evaluations of nonaqueous reprocessing methods for spent nuclear reactor fuel elements are being made in the Pyrochemical and Dry Processing Methods (PDPM) Program in an effort to determine chemical feasibilities within the constraint that the processes be proliferation-resistant.

The program for FY 1979 has been administratively divided into individual work packages, five of which are being done at Argonne National Laboratory (ANL). Each work package is being managed for conformance to established statements of work, program objectives, a cost plan, a milestone plan, and a management plan according to the Uniform Contractor Reporting System, DOE/DR-0001/1, dated February 1978, as required by the Department of Energy.

7.1 Management

C. H. Bean and S. Vogler (ANL)

The status of ternary-phase-diagram developments by the Colorado School of Mines, under subcontract to Rocky Flats, and by Babcock & Wilcox (B&W) was reviewed on August 13 and 14, 1979. The Colorado School of Mines group is studying the copper-rich portion of the copper-magnesium-uranium ternary phase diagram, which is of interest to the salt transport process development at Rocky Flats. The potential for locating a low-melting ternary eutectic in the region of 70 to 78% copper, 10 to 18% magnesium, and 7 to 15% uranium appears promising. Although support for this work by Rocky Flats is being terminated, the project will be continued by the Colorado School of Mines under the graduate studies program. The plutonium-uranium-zinc phase diagram studies at B&W are based on computer models developed under subcontract with Manlabs. Compositions of interest are being verified experimentally by differential thermal analysis with specimens encapsulated in tantalum. After termination of the PDPM Program, B&W will support further studies and development of the plutonium-uranium-zinc ternary system.

In response to a letter (dated August 7, 1979) from R. H. Bauer, Manager of the DOE's Chicago Operations Regional Office, to W. E. Massey, Director, ANL, relative to the PDPM Program, the requested actions have been taken for terminating the program. All contractors were notified by letter (dated August 13, 1979) of contract termination effective September 30, 1979, and were further instructed to complete all close-out activities and to prepare draft topical reports by September 30. Materials development efforts, proof-of-principle experiments, and separation process runs have been terminated. The draft topical reports for materials and process developments were approximately 80% complete by September 30. A property survey and equipment inventory was completed, and capital equipment items are now subject to standard property control and disposal procedures administered by the ANL Procurement Division. Plans were completed to finish the technical review and publication of all PDPM topical reports. The costs of program termination were determined; these

include the program overrun for FY 1979 and the close-out costs for FY 1980. Close-out costs will cover the documentation of all research and development efforts, including costs for the publication of topical reports, the cost of controlling government-owned capital equipment, and a contingency for contract close-out costs.

7.2 Engineering Analysis

7.2.1 Uranium-plutonium salt transport processing

The selective transfer of spent fuel constituents between liquid metals and/or molten salts was studied for both thorium-uranium and uranium-plutonium oxide and metal fuels. The chemical basis for the separation is the selective partitioning of actinide and fission-product elements between molten salt and liquid alloy phases. The partitioning is determined by the values of the standard free energy of formation of the chlorides of actinide elements and fission products. Elements to be partitioned are dissolved in one alloy (the donor alloy), oxidized when mixed with the salt, transported in the salt to a second alloy (the acceptor alloy), reduced, and finally dissolved in the acceptor alloy. The primary technical goal for uranium-plutonium salt transport processing was to develop a viable flowsheet for producing a proliferation-resistant product suitable for reactor use by pyrochemical means through coprocessing.

Salt transport process design [J. E. Hicks (Rockwell International, Rocky Flats)]. The turntable transport process (TTP) design is complete; detailed material and energy balances will be presented in a topical report.

Each stage of the mixer-settler continuous process (MSC) consists of two mixers and two settlers. The donor and acceptor metal streams move from stage to stage countercurrent to each other. The transport salt is captive within each stage and contacts the donor and the acceptor alloy in cross-current fashion. This flow pattern allows the MSC train to perform as if donor and acceptor alloys were immiscible phases in countercurrent contact. The mass transfer coefficients between donor and acceptor, calculated from known donor-salt and salt-acceptor equilibrium coefficients, allow the number of ideal stages to be calculated. For the reference fuel and a representative donor alloy, transport salt and acceptor alloy at a typical temperature (800°C), two equilibrium stages are required.

Proliferation study [J. L. Zoellner (Rockwell International, Rocky Flats)]. The uranium-plutonium salt transport process was examined to determine whether modifications to the process can be accomplished that will adversely affect the proliferation resistance.

The effects of recycle of core/axial blanket and radial blanket fuel were analyzed, but a suitable method of obtaining a 20% enrichment and a 99% recovery from blanket assemblies has not been found assuming that the same reagents are used for radial blanket assemblies as were used for core/axial blanket assemblies. The effect of increasing magnesium content of the uranium-plutonium donor alloy for reprocessing radial blanket fuel assemblies has been studied. As the magnesium content is increased, the enrichment does go up, but the corresponding plutonium recovery decreases. In all cases, the fission products transferred with the alloy are sufficient to keep the radiation level well above the minimum desired amount. In addition, the required mass of material to keep the magnesium in solution results in volumes which are too large for the 10 ft³ design vessel volume. Therefore, increasing the magnesium content of the donor alloys is not practical from a diversion standpoint.

If the core/axial blanket acceptor alloy product is recycled back through the process (under base case conditions) there is a slightly higher enrichment of the processed material. It may be possible that the enrichment could be significantly increased upon repeated recycle of this material.

During recycle of the various types of materials, if the initial conditions assumed fresh, uncontaminated salt, insufficient fission products remained in the alloys to maintain proliferation resistance in all cases. Using contaminated or spiked salts in all recycling, as well as regular processing, ensures that sufficient quantities of fission products are contained with the plutonium. Design provisions should be made to increase the difficulty for replacing the transport salts during operation. The use of vessel heels represents a second solution. The heel remaining in the bottom of the acceptor vessel could be sized to contain sufficient fission products so that even if a decontaminated alloy were introduced into the vessel, the resulting radiation level would meet the proliferation resistance criteria.

Zinc/cladding separation [R. L. Sandvig, G. A. Lambert, and S. J. Dyer (South Dakota School of Mines)]. A literature search on the nonaqueous separation of zinc from fuel rod cladding has been completed and a topical report will be issued as a separate document.

Computer model [W. A. Averill (Colorado School of Mines)]. The second generation computer model of the transport process (SALT-II) has been completed. There are some significant improvements incorporated into this version which include (1) a change in the method of equilibrating the solid alloy phases with liquid alloy phases (the routine which equilibrates the salt and alloy also contains the calculation for the liquid/solid alloy equilibration); (2) the allowance for heels in process vessels (which allows the model to simulate actual process operation when material is transferred from one vessel to another and small amounts of material are left behind); and (3) an allowance for multiple passes (which enables the examination of transient and steady-state behavior of the system).

7.2.2 Chloride volatility processing of thorium-based fuels **R. L. Bennett (Babcock and Wilcox)**

This study was made to determine the feasibility and proliferation resistance of a chloride volatility coprocess for the recovery of fissile material from thorium-based fuels.

An evaluation of the block flow diagram for the chloride volatility coprocess was completed. If either the volatilization temperature or the condensation temperature is altered, the fissile material can be separated from the fertile material; however, some highly radioactive fission products would be associated with the fissile material, would make the initial misappropriation of fissile material more difficult, and would add to the difficulty of converting the chloride to the metal. These factors increase the time and level of sophistication required for proliferation. If no process modifications occur, radioisotopes remain with the fuel throughout the process, which causes the finished fuel element to be radioactive.

7.2.3 Molten salt processes for nuclear fuel **Duane H. Smith and E. C. Douglas (ORNL)**

The first step in the PROMEX flowsheet for oxide fuels is the dissolution of the fuel into a molten mixture of $\text{LiCl}/\text{AlCl}_3$. It might be desirable to keep the volume of Al_2O_3 formed in this step to a minimum. According to Moore,¹ who studied the dissolution of

uranium oxide in KAlCl_4 , sparging of the melt with carbon chlorides reduced the amount of Al_2O_3 formed from $\frac{1}{3}$ to $\frac{1}{25}$ of the amount of Al_2O_3 produced without sparging. Accordingly, sparging of the $\text{LiCl}/\text{AlCl}_3$ melt with a carbon chloride gas has been proposed as a possible modification of the PROMEX flowsheet.

7.2.4 Molten tin process for reactor fuel

O. Krikorian, J. Grens, M. Coops, and W. Parrish (Lawrence Livermore Laboratory)

Recently, it has become clear that the molten tin process can produce separate product streams that present important advantages in terms of nuclear waste disposal. The process essentially produces five streams (see Figs. 7.1 and 7.2): (1) gaseous fission products (2) fission products that are the major decay heat producers, (3) fuel-rich actinides, (4) fuel-depleted actinides, and (5) fission products that are low-decay heat producers. The gaseous fission products (I_2 , Kr, Xe, HT), accompanied primarily by CO produced during the carbothermic reduction of oxide fuels, are in relatively concentrated form. This provides for relatively simple processing to concentrate the gaseous fission products prior to storage (if required). The fission product elements that are the main decay heat producers for the period of 10 to 1000 y are cesium, strontium, and samarium. Virtually all of the cesium and strontium and a large portion of the samarium can be removed in a metal volatilization step (see Fig. 7.2), which substantially reduces heat generation in the remaining fission products. The high- and low-decay heat fission products can be stored separately using different design concepts to accommodate the differences in heat generation rates. The actinide streams (if storage is required) would use yet different storage design concepts since they contain alpha-emitters which can cause severe radiation damage in solid host materials.

Fig. 7.1. Molten tin process flowsheet. (Courtesy Lawrence Livermore Laboratory)

Fig. 7.2. Fission product distribution during evaporation step of molten tin process. (Courtesy of Lawrence Livermore Laboratory)

7.2.5 Support programs

In addition to those efforts directly concerned with process development, there are other programs directed towards providing support for process development.

Material development for PDPM [R. M. Arons and J. Y. N. Wang (ANL)]. The corrosion of molybdenum-tungsten alloys in liquid zinc at 455°C for 1 year has been examined recently in Austria.² The alloys were produced by vacuum arc melting, or by powder metallurgy pressing and sintering. The resistance of these alloys to molten zinc was independent of the method of production. Resistivity of the Mo-30 W alloy is practically unlimited at this temperature. The Mo-10 W alloy shows measurable corrosion rates, but the weight loss of pure molybdenum is about 10 times as high as the Mo-10 W. The Mo-5 W alloy showed the highest corrosion rate of all tested specimens.

Tungsten sintering as an alternate method of fabricating large tungsten crucibles has been investigated. The activation of sintering by use of nickel or palladium has been documented.^{3,4} In this work, cold-pressed tungsten bars were impregnated with alcohol solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{PdCl}_2 \cdot \text{H}_2\text{O}$, followed by a drying cycle, and then firing in pure hydrogen for 5 to 240 min at temperatures from 850 to 1200°C. Increasing the amounts of activator metal strongly increased sintering kinetics up to an optimum activator concentration corresponding to one monoatomic layer of activator on the surface of the tungsten particles. The mechanism of sintering enhancement was apparently surface diffusion of tungsten on the activator surface. This conclusion was supported by the observation that the activation energy measured for enhanced sintering was well below that for tungsten volume diffusion and lay between that of surface diffusion and grain-boundary diffusion. No theory exists concerning why nickel or palladium has the power to extensively modify the surface of tungsten or the surface diffusivity. Segregation of the activators to the grain boundary and an embrittlement of the metal leading to intergranular fracture was also observed.

Fabrication of process-size refractory metal vessels [C. M. Edstrom, C. E. Baldwin, R. R. Corle, L. D. Johnson, and A. G. Phillips (Rockwell International, Rocky Flats)]. The current emphasis of this activity is to complete the service life testing of three fabricated vessels.

A topical report on the literature search for tungsten fabrication has been distributed. This report⁵ summarizes most of the methods for fabricating tungsten, such as sintering, rolling, extruding, spinning, joining, chemical vapor deposition, and plasma spraying.

A transfer line (1-in.-diam by 14-ft-long) made from Mo-30 W, as designed and manufactured by Metalwerk Plansee, would cost approximately \$12,000. The tube is made by drilling 24-in. lengths of 1.57-in.-diam rod, threading, and joining the lengths with a threaded pipe coupling. Thermo Electron (another refractory metal tube supplier) can gun drill the Mo-30 W in 10-ft lengths, which may reduce the manufacturing costs by eliminating some joints. Gun drilling would permit the use of rods that have a smaller outside diameter.

Analytical determination of uranium-plutonium-zinc phase diagram [J. E. Bullard, L. A. Smith, and T. A. Thornton (Babcock and Wilcox)]. This phase diagram is important for the zinc distillation process (also referred to as the Exportable Pyrochemical Process, EPP). In this process, the fuel is exposed by dissolving the cladding in molten zinc, followed by removal of the liquid zinc containing dissolved stainless steel. The residual fuel oxide is reduced by calcium and dissolved in molten zinc. The gaseous and volatile fission products are separated from the fuel, and partial removal of the rare earth fission products is effected by titrating the zinc with a molten salt. A limited increase in concentration of the plutonium is accomplished by a high-temperature zinc distillation step, where about one-half of the uranium precipitates. The remaining liquid zinc containing the plutonium and the remainder of the uranium and noble metal fission products is then cooled to precipitate uranium, plutonium, rare earths, and about one-half of the noble metals. After removal of the bulk liquid zinc, the remaining zinc is removed by distillation, and the solidified and cast product from this step is oxidized for use as proliferation-resistant refabricated fuel.

The thermodynamic analysis of the phase relationships in the uranium-plutonium-zinc system has continued using the HP-67 calculator programs described by Brewer.⁶ Each program uses different starting data and different assumptions to calculate the constants which characterize the phases; therefore, some care is required in selecting the proper program. These programs can be used to analyze the existing binary-phase diagrams and will allow the determination of constants which characterize all of the phases on the three binaries. These constants can then be averaged to allow the estimation of the excess partial molal Gibbs energy of the components in the ternary mixtures. From this information, phase boundaries can be calculated.

The method given above has three basic limitations: (1) it does not account for any ternary compounds, (2) the use of a two-term power series in the programs gives limited accuracy, and (3) averaging of the binary data to calculate free energies for ternary mixtures is an approximation.

A ternary phase diagram (Fig. 7.3) for the zinc-uranium-plutonium system was developed by Manlabs.⁷ The exact method by which the phase boundaries are calculated by Manlabs is proprietary, but it is limited, like the Brewer method, to using only a quadratic and cubic term and in averaging binaries to calculate free energies for ternary mixtures. Ternary compounds, when they are known to exist, can be included in the calculation, but the program will not predict such compounds. The calculated phase diagram (Fig. 7.3) is therefore not expected to be accurate in detail, but it will be valuable in early process feasibility studies and will aid in the selection of compositions for experimental melts.

Fig. 7.3. Ternary phase diagram for the zinc-uranium-plutonium system. (Courtesy Babcock and Wilcox)

Engineering analysis of the EPP fuel cycle [L. J. Jones, L. F. Grantham, and R. C. Hoyt (Rockwell International, Atomics International)]. Engineering evaluations have been performed for portions of a fast breeder reactor (FBR) fuel cycle utilizing pyrochemical reprocessing. Results are summarized for (1) conversion of the metallic uranium-plutonium alloy reprocessing product to the oxide, (2) refabrication of the oxide product, and (3) waste management for the pyrochemical reprocessing plant. In addition, a preliminary economic evaluation is included for uranium-plutonium alloy conversion to a mixed oxide (MOX) fuel, reprocessing waste management, and decontamination and decommissioning of the EPP facility.

The product of the pyrochemical reprocessing method is a uranium-plutonium alloy product that must be oxidized prior to pelletization and refabrication into fuel elements. The uranium-plutonium alloy consists of about 75 wt % uranium, about 25 wt % plutonium, and from 1 to 4 wt % rare earth and transition metal fission products. Although a literature survey indicates that it is feasible to oxidize this uranium-plutonium alloy with air, the sinterability of the oxide product must be demonstrated. Air oxidation of uranium metal generally produces an unsinterable oxide powder, whereas steam oxidation of uranium metal produces a powder of limited sinterability.⁸ Since steam oxidation is too slow for commercial application, a fuel cycle utilizing the EPP would probably use air oxidation of the alloy product followed by activation to enhance sinterability.^{9,10} Activation can be achieved by oxidizing the UO_2 to U_3O_8 at low temperatures and reducing the U_3O_8 to UO_2 with hydrogen in an inert-gas mixture.

Plutonium in the uranium generally enhances the air oxidation rate of the alloy; some fission products enhance oxidation and others retard the oxidation rate. Air oxidation rate studies of uranium-plutonium alloy and uranium-fission product alloys indicate that a uranium-plutonium-fission product alloy will probably oxidize more rapidly than pure uranium. Thus, it appears that air oxidation of the EPP product is feasible, but further development is required to optimize the oxidation conditions and the conditions required to activate the oxide product into a sinterable powder.

One important consideration in choosing oxidation conditions for the EPP alloy is the volatilization of ruthenium, since it is one of the major fission products contributing to the radioactivity of the fuel. Low volatilization of ruthenium is desired to ensure adequate proliferation resistance, but the behavior of ruthenium under oxidizing conditions at various temperatures is not yet understood, and the literature contains conflicting data. Ruthenium volatility has been shown to be different for waste of different composition,¹¹ and this probably accounts for some of the discrepancies in the literature. Significant quantities of ruthenium have been reported to be volatilized during spray calcination at temperatures from 350 to 500°C but not at temperatures near 700°C.¹² In another report, ruthenium was significantly volatilized during spray calcination at temperatures from 400 to 800°C¹¹ and during voloxidation tests at 450 to 750°C.¹³ Data on ruthenium volatilization during air oxidation of uranium-fission metal and oxide skulls, however, showed no significant volatilization in the temperature range from 700 to 900°C.¹⁴ Many of the tests also involved successive oxidation-reduction cycles without loss of ruthenium. Ruthenium was not even volatilized from oxidized skulls when heated in oxygen at the lower temperatures of 100 to 400°C. Therefore, it was concluded that ruthenium was not expected to be a problem during the oxidation of uranium-fission metals and fission product skulls.

Although it is not possible to predict the behavior of ruthenium during the EPP alloy-to-oxide conversion process because of the conflicting data in the literature, it could be expected to be similar to that occurring during uranium-fission metal and skull oxidation. If this is true, volatilization of ruthenium during EPP alloy oxidation in air at temperatures of 700 to 900°C will not be significant.

The EPP facility reprocessing waste consists primarily of cladding sponge, end hardware, metal alloys, salt mixtures, volatile fission products, water from oxide activation, and CO₂ from calcium recovery. The guidelines for this evaluation specified that the contaminated uranium product would also be treated as waste. A preliminary engineering study indicated that conventional waste management practices can be utilized in most cases. By placing the waste salt in a canister containing cladding, end hardware, and metallic processing wastes, the resultant thermal conductivity of the layered mixtures was increased sufficiently to reduce the centerline canister temperatures to acceptable levels (<400°C). The contaminated uranium sponge can be melted and cast in a disposable canister. A small amount of molybdenum was included in the uranium to reduce any fire hazard associated with storage of uranium metal. The radioactivity of the contaminated uranium product is low enough to maintain the canister centerline temperature at acceptable levels. The inert gas volatile fission products can be separated from the waste gas by cryogenic or fluorocarbon collection methods and stored in compressed cylinders. The volatile iodine can be converted to and disposed of as nonvolatile iodates or zeolites by conventional processes. The water produced during oxide powder activation will not be contaminated with tritium and can be disposed through the storage pool wet waste system. Similarly, the CO₂ produced during calcium recovery will not be contaminated with ¹⁴C and can be released up the stack. The management of wastes from the EPP facility should be much easier than the management of waste produced by a conventional Purex reprocessing plant because nitrogen oxides are not present in the off-gas and because the volatile fission products are more concentrated.

A preliminary engineering study was made of refabrication of the EPP product after conversion to a sinterable powder. A flowsheet was developed which used conventional pressing, sintering, and refabrication technology but was modified so that the fuel could be refabricated remotely behind shielded concrete walls. Operation of the proposed facility on a 300 d/year basis would produce 117 t of FBR driver fuel per year. It was assumed that

virgin depleted uranium oxide would be used for the blanket fuel and that radial blanket fuel assemblies and axial blanket fuel pellets used in driver fuel rods would be produced offsite. Axial blanket pellets would be transferred to the remote handling refabrication facility for incorporation into the FBR driver fuel assemblies. It was assumed that the refabricated fuel assemblies could be stored in the same EPP facility storage pool that is used to store spent fuel awaiting processing.

Preliminary cost estimates of alloy conversion to oxide, reprocessing, waste management, refabrication of the oxide product, and decontamination and decommissioning of the EPP facility have been made and are summarized in Table 7.1.

Table 7.1. Summary of capital and operating costs

Portion of fuel cycle	Capital costs (\$10 ⁶)	Operating costs (\$10 ⁶ /year)
Alloy conversion to oxide	7.3	0.9
Reprocessing waste management	12.0	3.4
MOX refabrication	156.0	18.0
Decontamination and decommissioning		5.6

7.3 Separations Processes

7.3.1 Salt transport processing

Uranium-plutonium salt transport processing [J. B. Knighton, C. E. Baldwin, W. A. Averill, M. Bracco, M. F. Boyle, S. J. Dyer, J. E. Hicks, G. A. Lambert, T. D. Santa Cruz, R. L. Sandvig, S. P. Sontag, and J. L. Zoellner (Rockwell International, Rocky Flats)].

Proof-of-principle studies. The first equilibrium experiment was made to measure the partitioning of Pu, U, FP-3's (using Am as a stand-in) and FP-4's (with Zr as a stand-in) between the molten salt and alloy phases that represent the FP-3/donor alloy segment of the salt transport process. The experiment involved a molten salt composed of 6.4 wt % MgCl₂, 17.8 wt % KCl, and 75.8 wt % CaCl₂ and a liquid alloy composed of 79.1 wt % Cu, 4.6 wt % Mg, 7.2 wt % Pu and Am (combined), 7.9 wt % U and 1.2 wt % Zr. Salt and alloy samples were obtained from each phase at each equilibration temperature from 810 to 930°C. The distribution coefficients (defined as the ratio of the concentration of a species in the salt phase to that of the same species in the alloy phase) were calculated from the sample results and are shown in Table 7.2. At 810°C, the distribution coefficients can be compared to the estimated distribution coefficients used in the computer modeling of the salt transport process.

The FP-3's distribution coefficient (assumed from the americium measurements) is approximately an order of magnitude different than the value used in modeling of the process. This difference may be caused by the use of americium rather than cerium as the FP-3 stand-in. The distribution coefficients for uranium and plutonium are close to the estimated values. The increase in the americium distribution coefficient as the temperature is increased was not expected and will have to be verified by future experiments. Transfer of the FP-4 stand-in (Zr) from the alloy to the salt phase was not evident from the data.

Table 7.2. Comparison of experimental distribution coefficient values with estimates for a typical FP-3/donor alloy system

Temperature (°C)	Experimental distribution coefficients, K_d		
	Am	U	Pu
810	0.44 (10.7) ^a	0.0076 (0.0015) ^a	0.024 (0.0317) ^a
830	0.58	0.0020	0.016
855	0.46	0.0065	0.045
855	0.74	0.0022	0.028
930	0.94	0.0011	0.029

^aEstimates in parentheses; the americium, uranium, and plutonium data are compared with an estimate for cerium.

The second proof-of-principle study was made to determine the distribution coefficients of americium, plutonium, and uranium for the uranium-plutonium/donor alloy system. The alloy phase was copper-magnesium and the salt phase was $\text{MgCl}_2\text{-MgF}_2$. Uranium was added to the alloy to a concentration of 10 wt %. The alloy and salt were heated, and samples were obtained to provide a base measurement for the experiment. Plutonium and americium were added to the molten salt and liquid alloy; additional samples were obtained from this mixture.

Analytical results indicated that the amounts of plutonium and americium transferred from the alloy phase to the salt phase were independent of temperatures in the range from 800 to 870°C. The uranium did not show an inclination to transfer. The estimated distribution coefficients are compared with those found experimentally (Table 7.3).

Table 7.3. Comparison of experimental distribution coefficient values with estimates for a typical uranium-plutonium/donor alloy system

Metal	Distribution coefficients, K_d	
	Experimental	Estimated
Am	≈ 9	600 ^a
Pu	≈ 1	2.1
U	≈ 0.03	0.41

^aEstimated for cerium for which americium was considered a stand-in.

Molten salt purification laboratory. The black salt studies have focused on the metal (or alloy) contained by the salts or black salts as reported in the electrorefining literature of plutonium. The modes of impurity containment range from simple entrainment through the formation of colloidal metallic fogs ("metallnebels") to the formation of sub-halide compounds. This problem has been recognized in the literature for some time,¹⁵⁻¹⁹ and the

various modes for alloy containment find support, but are not proven, by the physical properties of the salts. In the electrorefining literature for plutonium, there are terms "black solid," "black material," and "black salt" used. These reports come from several laboratories including Hanford,²⁰ Savannah River,²¹ and Rocky Flats.²² The survey has revealed that by varying the average charge density on the cations in the salt, greater solvation of solutes can be accomplished and more complete consolidation of metals in the salt can be made.

Calcium chloride is a major ingredient in many of the salt systems used in the PDPM Program. The ability of calcium chloride to dissolve calcium oxide is important to the salt transport studies. Reagent anhydrous calcium chloride contains not less than 96% CaCl_2 , nor more than 2.0% magnesium and alkali salts (as sulfates), and not more than 0.02% Ca(OH)_2 . The remaining impurity in calcium chloride is water from the deliquescence of calcium chloride. The presence of water has a deleterious effect when the calcium chloride is fused (i.e., at the temperatures needed for molten salts, the water absorbed by the salt reacts with the calcium chloride producing calcium oxide and hydrogen chloride). Samples of a reagent grade batch of anhydrous calcium chloride taken prior to and after fusion contained calcium oxide contents of 170 and 6400 ppm respectively.

The calcium oxide content can be reduced by sparging the molten salt with anhydrous hydrogen chloride²³ or by contacting the molten salt with a reductive liquid alloy such as cadmium-magnesium.²⁴ The buildup of calcium oxide could be prevented by removing the water prior to fusion of the salt.^{23,25} The sparging technique has been tested and can reduce the calcium oxide content from 6400 to 320 ppm. Contacting the salt with a liquid alloy results in removal of calcium oxide to the 2000 ppm level. A vacuum drying technique leaves about 300 ppm calcium oxide in the salt after it is fused.²⁵

Uranium-copper-magnesium ternary studies. The first trial run was made using a magnesium-copper binary alloy consisting of 2 wt % magnesium and 98 wt % copper, with pure copper as a reference. The alloy did not melt completely as evidenced by the differential thermal analysis (DTA) information and by physical observation.

A second trial run was made using a 5 wt % magnesium and 95 wt % copper alloy, with pure copper as a reference. A eutectic mixture of CaCl_2 and CaF_2 was placed on top of the alloy to prevent the escape of excessive magnesium vapor from the crucible. These data were compared to the phase diagrams reported in the literature; some disagreement was noted. The composition of the prepared alloy was apparently not maintained during the meltdown. A shift of 2% toward the copper-rich side was indicated and later confirmed by atomic absorption analysis.

A copper-uranium master alloy composed of 74 wt % copper and 26 wt % uranium was formulated to mix with the copper-magnesium alloy for preparing the ternary alloys. The first ternary data point was obtained using an alloy composed of 17.5 wt % magnesium, 12.5 wt % uranium, and 70 wt % copper. The first isopleth developed was for 5 wt % uranium. Data points were obtained for magnesium compositions from 2.5 to 20 wt %. These were based upon the compositions of the copper-uranium master alloy and the copper-magnesium master alloy. The amount of copper and magnesium will be determined by atomic absorption; the uranium will be determined by x-ray fluorescence. Currently, work is being done on the 10 wt % uranium isopleth.

Thorium-uranium salt transport processing [M. Krumpelt, M. Ader, R. Barletta, J. Bates, T. Gerding, D. Kroeck, and J. Meisenhelder (Argonne National Laboratory)].

Solubility studies. The main process separation step requires that thorium be partitioned between plutonium which is soluble in cadmium-magnesium alloys and uranium

which is insoluble in cadmium-magnesium alloys. Thorium solubility measurements have been made for the ternary system thorium-magnesium-cadmium to permit the selection of proper process conditions. Studies are continuing to identify the solid phases that precipitate from solutions of different compositions; the ultimate goal is to define the phase diagram.

Solubility of thorium in cadmium. Measurements of thorium solubility in liquid cadmium at temperatures between 327 and 568°C were reported last quarter.²⁶ These solubilities represent liquidus compositions of the binary phase diagram, the equilibrium solid phase being ThCd_{11} . The solubility data have now been extended to 658°C and show that ThCd_{11} decomposes peritectically at about 568°C to an unidentified, less cadmium-rich intermediate phase. The experimental results are plotted as log wt % thorium solubility vs reciprocal absolute temperature (Fig. 7.4). A dashed straight line representing a least-squares fit of the solubility data is also included.²⁷

Fig. 7.4. Thorium solubilities in cadmium and cadmium-magnesium. (Courtesy Argonne National Laboratory)

Intermediate phases in the cadmium-thorium system. Experiments to define prominent features of the cadmium-thorium binary phase diagram are in progress. Electron microprobe analysis has been used to obtain preliminary information concerning the composition of intermediate phases. The results of three of the capsule experiments are summarized in Table 7.4.

Table 7.4. Electron microprobe analysis of cadmium-thorium alloys

Capsule	Atomic Cd-Th ratio	Heated		Phase	Cd-Th analyses (wt %)
		°C	Time		
5	13	545	17 d	(1)	Cd(84) – Th(16)
				(2)	Cd(100) – Th(<0.5)
				(3)	Cd(64-75) – Th(36-25)
1	7	1000	21 h	(1)	Cd(83) – Th(16)
				(2)	Cd(59-64) – Th(40-36)
7	4	650	14 d	(1)	Cd(<0.2) – Th(100)[unreacted Th]
				(2)	Cd(100) – Th(<0.4)
				(3)	Cd(74-66) – Th(26-34)

Cadmium-magnesium-thorium system. Additional information on the cadmium-magnesium-thorium ternary phase diagram is being obtained. Three different regions of the ternary system were selected for studies on liquidus contours, equilibrium intermetallic compounds, and eutectic compositions. A semi-log plot of the thorium solubilities vs reciprocal temperature is shown in Fig. 7.4 as a straight line. The slope of this line approximates thorium solubility in pure cadmium. This suggests that, despite the presence of about 11 wt % magnesium, the solid phase precipitating in this region of the ternary diagram may be ThCd_{11} .

Cadmium-magnesium-thorium phase diagram. A preliminary ternary phase diagram has been drawn (Fig. 7.5) based on available information. In the thorium-magnesium binary system only one compound (ThMg_5) is known.²⁸ In the thorium-cadmium binary system, ThCd_{11} has been positively identified and preliminary evidence has been obtained for ThCd_6 , $\text{ThCd}_{3.5}$, and ThCd_2 . No compounds have been reported for the cadmium-magnesium system. Since the slope of the thorium solubility line in Fig. 7.4 was similar to the one for ThCd_{11} in the binary system (indicating that ThCd_{11} was precipitating), a tie-line has been drawn between ThCd_{11} and Mg. Other tie-lines have been tentatively drawn between ThMg_5 and the various thorium-cadmium compounds. The ternary eutectic compositions are indicated by the squares in Fig. 7.5. The dashed line connects these three points and also the known eutectic points in the thorium-cadmium and thorium-magnesium systems. This line is a first-order estimate of ternary eutectic compositions. The circles represent liquidus compositions in the ternary system at different temperatures. The line running above the eutectic line represents a 580°C liquidus contour. The phase diagram indicates that the thorium solubility increases with increasing magnesium content of the ternary alloy as reported earlier.²⁹

Fig. 7.5. Preliminary phase diagram for the cadmium-magnesium-thorium system. (Courtesy Argonne National Laboratory)

Differential scanning calorimetry (DSC). The thermogravimetric-differential thermal analysis (TG-DTA) unit is still not properly installed, but it can be used to measure heats of transition and to note heat changes. Problems exist in measuring the temperature of these events. The instrument has been calibrated for each mode of operation using NBS reference standards for the temperature calibrations and high-purity metal samples for the heats of fusion calibrations. The melting temperatures were consistently low with the deviation increasing at higher temperatures. The heats of fusion values were consistently high and led to the establishment of a correction factor. The instrument currently is being used to determine heats of reaction for the peritectic decomposition of ThCd_{11} and to aid in the establishment of the thorium-cadmium-magnesium and thorium-cadmium phase diagrams.

Reduction of thorium oxide. The reduction of thorium dioxide is an essential step in the reprocessing of oxide fuels. Low-fired thoria pellets are difficult to reduce, and only 5 wt % of an initial charge is reduced after 4 h at 675°C . Material obtained from a reactor is probably of intermediate difficulty to reduce.

Seven factors must be considered when evaluating the reduction process: alloy composition, fuel type, flux composition, process temperature, mixing parameters, metal loading, and oxide loading. Two types of experiments were planned to identify which one of these factors is most important in controlling the reduction rate.

The first set of nine experiments using thoria powder was made to determine the effect of final thorium loading in the metal alloy, final calcium oxide loading in the salt, and the temperature. These factors became the independent variables of a factorial experiment, and the other factors were held constant. The rate of reduction was the dependent variable.

In each of the experiments the total amount of reduction was less than expected, with only about 10% of the thoria being reduced. Previous reductions with calcium, using a copper-magnesium alloy and a slow stirring rate, indicated at least 60% reduction.³⁰ In addition, all the reduction that occurred appeared to take place during the first hour. This might indicate that no reduction occurred and that the thorium appearing in the alloy was from ThO_2 that passed through the filter.

The second set of reduction experiments will be done with low-fired ThO_2 pellets obtained from Westinghouse. These experiments are designed to study the effect of mass transfer between the salt and alloy and between the salt and pellet.

Molten salt recycle, electrolysis of calcium oxide in molten salt. Studies are continuing on the electrolysis of calcium oxide in fused CaCl_2 - CaF_2 using a molten metal cathode. The aim of these experiments is to develop a process to reduce the large volume of salt waste in pyrochemical flowsheets. The cathodic reaction in this process produces calcium metal for recycle while the anodic reaction on graphite yields a waste stream of CO/CO_2 gas. The salt medium after this electrolysis would be available for recycle.

Previous experimental studies²⁷ have shown that, while calcium oxide reduction did occur, the observed decomposition potential of calcium oxide using a carbon anode was not as low as that predicted from thermodynamic calculations. Additional experiments were performed under conditions of increasing and decreasing potential to ascertain the accuracy of the previously reported decomposition potentials and to reconcile the current-potential data obtained during electrolysis experiments. The two systems chosen for study at 690°C were 15 wt % CaF_2 - CaCl_2 and 15 wt % CaF_2 - CaCl_2 to which 12.5 g (5 wt %) CaO had been added. The current-potential curves obtained are shown in Fig. 7.6. The decomposition potentials obtained in these experiments are given in Table 7.5. While there was little variation in the observed decomposition potentials and good agreement was obtained with data previously reported, much lower currents were observed, especially at low potentials when the voltage was decreased. This difference could account for the difference between the final electrolysis current and current-potential data of the previous electrolysis experiments. In future experiments, current-potential data will be taken by increasing the applied potential and by allowing time for the current to reach an equilibrium value.

Fig. 7.6. Current-potential curves taken with either increasing or decreasing potential. Data points represent average equilibrium values. (a) 15 wt % CaF_2 - CaCl_2 , increasing potential; (b) 15 wt % CaF_2 - CaCl_2 , decreasing potential; (c) 15 wt % CaF_2 - CaCl_2 plus 12.5 g (5 wt %) CaO , increasing potential; (d) 15 wt % CaF_2 - CaCl_2 plus 12.5 g (5 wt %) CaO , decreasing potential. (Courtesy Argonne National Laboratory).

Table 7.5. Decomposition potentials for 15 wt % CaF_2 - CaCl_2 salt systems

	E_d (V)	
	Without CaO	With 5 wt % CaO
Increasing potential	3.01	2.38
Decreasing potential	3.08	2.39

An additional series of electrolysis experiments was performed in a molten fluoride salt consisting of 40 wt % LiF , 22 wt % CaF_2 , and 38 wt % SrF_2 to corroborate the CaO decomposition potentials previously measured in CaF_2 - CaCl_2 , thus eliminating possible contributions of CaCl_2 decomposition to the measurements. As with experiments in molten CaCl_2 salts, current-potential data were taken in molten salt alone and in the salt mixture to which 5 wt % CaO had been added using either a graphite or platinum anode and a molten 35 wt % magnesium-copper alloy as a cathode. Data were taken by increasing the potential and allowing an equilibrium current reading to be obtained. Data were taken at temperatures of 780 and 810°C. Current-potential data obtained in the absence of calcium oxide indicated a fluoride salt decomposition potential of 4.8 to 5.3 V with either a graphite or platinum anode. This result compares reasonably well with the theoretical decomposition potentials of the various component salts based on free energy data at 1000 K. With the addition of approximately 5 wt % calcium oxide to the system, the decomposition potential on graphite anodes at 780°C was approximately 2.3 V; this value is nearly identical to that obtained for calcium oxide electrolysis at 775°C in a 15 wt % CaF_2 - CaCl_2 solution using a graphite anode.²⁷

The results of these experiments using molten fluoride salts indicate strongly that previous assignments of calcium oxide decomposition potentials in the CaCl_2 - CaF_2 medium were correct and that the separation of the calcium oxide decomposition potential from that of CaCl_2 is possible by using a carbon anode despite the fact that this value is higher than anticipated based upon free energy of formation data. Experiments performed by Thompson and Kaye³¹ on the decomposition of calcium oxide in a CaF_2 - SrF_2 salt mixture using graphite and platinum anodes indicated little difference between calculated and observed decomposition potentials, and hence, no overpotential for the calcium oxide electrolysis on graphite in their system.

7.3.2 Molten salt processes applied to nuclear fuels

Duane H. Smith and E. C. Douglas (ORNL)

The study of the dissolution of ThO_2 and UO_2 in molten $\text{LiCl}/\text{AlCl}_3$ mixtures has now been extended to a reaction temperature of 610°C.

The experiment was designed to reach the minimum obtainable (or equilibrium) concentration of AlCl_3 , consequently, very long reaction times of up to 120 h were used. The temperature of 610°C was chosen because it is the lowest possible temperature to which the system would be exposed in the next process step, and because it was expected to exceed the liquidus temperature of any composition which would be reached in either the $\text{ThCl}_4/\text{LiCl}/\text{AlCl}_3$ or the $\text{UCl}_4/\text{LiCl}/\text{AlCl}_3$ phase diagrams.

The solubility data for both UO_2 and for ThO_2 (which will be reported separately) show that equilibrium was obtained in less than 48 h and greater than 95% of the UO_2 dissolved. Approximately the same fraction of the ThO_2 dissolved, although the analytical scatter was considerably greater for ThO_2 than for UO_2 . At equilibrium, the molten salt solutions contained approximately equimolar amounts of UCl_4 or ThCl_4 and LiCl , and about 3 mole % AlCl_3 . These results show that very high concentrations of UCl_4 and ThCl_4 and low concentrations of AlCl_3 can be obtained. Similar results can be expected for plutonium.

The process acceptability of the dissolution reaction at 610°C was demonstrated by using high-fired sol-gel microspheres of UO_2 ($195 \pm 15 \mu$ in diam) or of ThO_2 (350μ) sealed in quartz tubes with a Li/AlCl_3 mixture for reaction times of up to 8 h. For both urania and thoria, greater than 90% of the actinide oxide dissolved and reached equilibrium within 2 h. The speed and ease with which the ceramic ThO_2 dissolved was surprising in view of the great difficulties previously reported by various workers in attempts to dissolve ThO_2 by other means.³² These findings show that the rate, as well as the thermodynamics, of the $\text{LiCl}/\text{AlCl}_3$ dissolution meets process requirements.

7.3.3 Molten tin process for reactor fuels

O. Krikorian, J. Grens, M. Coops, and W. Parrish (Lawrence Livermore Laboratory)

Nitridation of uranium/plutonium mixtures in tin. A nitriding run was completed on a ^{238}U - ^{239}Pu mixture in molten tin. The reaction mix was composed of 50.2 g Sn, 1.5 g Ca (metal shot), 8.0 g U (3.2-mm-diam rod) and 1.74 g Pu. All metals were clean and shiny. Nitriding was carried out in a graphite reactor at a temperature of 1900 K under about 680-torr nitrogen pressure for 2 h. The product was a solid brittle metallic ingot that was very adherent to the graphite walls. It was remelted in a stainless steel vessel and pressurized with argon to drive out the molten tin through a porous carbon filter. The remaining nitride phase was dissolved in nitric acid and analyzed by mass spectrometry. It showed a ^{238}U - ^{239}Pu ratio of 10.14 compared to a ratio of 4.88 in the initial melt before nitriding. Thus, for these conditions of nitriding, uranium tends to become enriched in the nitride phase and plutonium tends to remain in the liquid tin phase.

Nitridation of thorium-uranium mixtures in tin. Experimentation to explore the separation of thorium from uranium by nitriding thorium-uranium mixtures dissolved in molten tin was initiated. Nitriding seems to be a reasonable approach for separation considering that thorium nitride is substantially more stable than uranium nitride. Experiments were made to test the hypothesis that thorium will nitride under conditions where uranium will not. In the first run, a composition of 50 g tin, 1 g uranium, and 1 g calcium (included as a catalyst) was subjected to a temperature of 1900 K under stagnant nitrogen to explore conditions at which uranium will not nitride. A variety of nitrogen pressures was used from 304 to 704 torr. No nitrogen uptake was observed under any of these conditions. (If as much as 6% of the uranium had nitrated, it should have been detected.) It was surprising that nitriding did not occur at the highest pressure (705 torr), since in earlier tests where higher uranium contents were used the reaction went to completion.

In the second experiment, 9 g of thorium was added to the mixture of 50 g tin, 1 g uranium, and 1 g calcium from the first experiment and then nitrated under 395-torr nitrogen for 2 h at a temperature of 1880 K. The nitriding rate for the thorium was found to be 6% per h. The nitriding rate of thorium in tin, in the absence of uranium, was tested using a mixture of 9 g thorium, 1 g calcium, and 50 g tin nitrated at an initial N_2 pressure of

674 torr and at a temperature of 1900 K. The nitriding was found to be nearly linear with time and was complete in 5.3 h.

A nitriding run was made using a mixture of 5.8 g uranium, 5.8 g thorium, and 50 g tin without any calcium catalyst present. The rate of N_2 uptake for a 1 h run at a temperature of 1900 K and 700-torr initial pressure was 10.5-torr per h. These results are not sufficient to test the hypothesis that thorium will nitride under conditions where uranium will not. Hopefully, more definitive results should become available when a filtration unit becomes operational for separating the nitride phase for the analysis of the uranium-thorium ratio.

7.3.4 Support programs

Material development for PDPM. [R. M. Arons, J. Y. N. Wang, D. J. Dorman, J. T. Dusek, and L. Marek (ANL)].

Metallic materials. A rocking furnace is in use to expose an entire test specimen to both molten metal and salts at a rate of six cycles per min. The exposure occurs within a $\frac{3}{4}$ -in.-diam tantalum tube. Furnace-dried $CaCl_2$, KCl, and zinc are loaded into the tube along with molybdenum test specimens. Both as-rolled and recrystallized TZM (Mo containing 0.5% Ti, 0.07% Zr, and 0.01% C) specimens have been exposed to a mixture of molten zinc and $CaCl_2$ -KCl salt at a temperature of about 800°C. The as-rolled material contained a fine dispersion of precipitates. After about 120 h of testing under an argon atmosphere, both specimens displayed higher corrosion rates than pure molybdenum under similar test conditions. Deep grain-boundary penetrations in the recrystallized specimen were clearly visible. The TZM alloy will be excluded from further consideration as a PDPM material.

The energy-dispersive x-ray emission spectrometry technique has been widely used for the analysis of post-test corrosion specimens, but because of problems from overlapping of adjacent lines in this technique, ambiguous results are often obtained. To overcome this problem, an evaluation of penetration and diffusion of molten metal species into the base metal by the wavelength-dispersive x-ray emission spectrometry has been attempted. This technique features extremely high wavelength resolution that permits the desired peaks to be clearly separated.

A Mo-30 W alloy was recently exposed to molten zinc and $CaCl_2$ -KCl at a temperature of 800°C for 120 h. The specimen was sectioned and the newly exposed area is being analyzed by the wavelength technique to determine the zinc diffusion as a function of distance from the surface exposed to molten zinc.

Ceramic materials. Five SiC samples, prepared by different methods, were exposed for 120 h at a temperature of 800°C in a mixture of molten zinc and fused $CaCl_2$ -KCl. The sample produced by chemical vapor deposition and three of the hot-pressed samples showed negligible weight loss. Scanning electron microscopy (SEM) showed no evidence of corrosion or of infiltration of the corrodents into the SiC. The fifth sample showed a 1% weight gain, and a SEM analysis showed some porosity, but no apparent corrosion products were seen. Although there may have been a slight infiltration of corrodents or moisture, x-ray analysis showed no evidence of zinc, calcium, or potassium, and moisture retention is unlikely since the sample was baked at 120°C in vacuum prior to weighing.

A similar tested Si_2ON_2 specimen showed a 5% weight loss which corresponds to a corrosion rate of 146 mils/year. Visual observation of the surface showed a color change from light gray in the virgin material to dark brown in the exposed material. The SEM and x-ray analyses showed a corrosion product rich in either copper or tantalum (the two

elements are virtually indistinguishable in energy-dispersive analysis). Since there is no potential source for copper, one must conclude that tantalum from the corrosion test apparatus hardware formed a compound or solution with the Si_2ON_2 .

A wide range of other ceramic materials has been tested, and the results are summarized in Table 7.6. As indicated, all ZrB_2 and ZrB_2 -SiC composite materials formed thick surface corrosion layers that easily spalled and showed multiple spallation layers as indicated in Fig. 7.7. The existence of more than one spalled layer indicates that corrosion – not thermomechanical transients – was the cause. The more promising ceramics are MgAl_2O_4 , Al_2O_3 , AlN , HfB_2 , Y_2O_3 , BeO , and possibly some Si_3N_4 formulations. Tests performed earlier showed SiC and graphite to also be resistant to the zinc and salt environment.

Plasma-sprayed tungsten. Two 7.62 cm $\times$ 7.62 cm (3 in. $\times$ 3 in.) cylindrical crucibles were formed by plasma spraying tungsten on a graphite mandrel. The crucibles were sent to Rocky Flats for heat treating where they were infiltrated with nickel nitrate, heat treated in pure H_2 for 1 h at 100°C and 3 h at 1300°C, and then subjected to a critical evaluation and corrosion testing. Dimensional changes upon firing included (1) 3.51 to 4.16% shrinkage in height, (2) 3.35 to 3.46% shrinkage in diameter, and (3) 25.7 to 31.4% shrinkage in wall thickness. These results are in agreement with previous findings that most consolidation occurs in the direction of prior spraying.

Table 7.6. Corrosion results for selected ceramics

Material	Form	Weight loss (%)	Surface loss		Comments
			mils/120 h	mils/year	
MgAl_2O_4	Hot pressed	0.18	0.10	7.3	
MgO	Sintered	24.38	<i>a</i>	<i>a</i>	Gross surface attack
MgO	Hot pressed	3.25	3.5	252	Gross surface attack
Al_2O_3	Refractory brick	0.44 ^b	0.24	17.2	
Al_2O_3	Hot pressed	0.047	0.059	4.3	
Al_2O_3	Hot pressed	0.083	0.057	4.2	
ZrO_2	Sintered	3.86	2.1	155	
ZrB_2	Hot pressed	7.49	3.5	258	Spalling surface product
ZrB_2 -SiC	Hot pressed	2.49	1.2	85.8	Spalling surface product
ZrB_2 -SiC	Hot pressed	8.61	4.9	359	Spalling surface product
ZrB_2 -SiC	Hot pressed	5.73	3.6	263	Spalling surface product
ZrB_2 -SiC	Hot pressed	65.1	30.8	2245	Thick surface product
Si_3N_4	MgO hot pressed	2.77	1.5	111	
Si_3N_4	Y_2O_3 hot pressed	1.08	0.7	52.9	
AlN	Hot pressed	0.10	0.045	3.3	
HfB_2	Hot pressed	0.77	0.45	33.1	Spalling surface product
Y_2O_3	Hot pressed	0.0013	0.001	0.056	
BeO	Hot pressed	3.16	0.50	36.4	

^aGross pitting and internal attack; surface loss rate meaningless.

^bSample was friable, and the weight loss may have been mechanically induced.

Fig. 7.7. Specimen after 800°C and 120-h exposure to Zn and CaCl₂-KCl. Wire wrapped around specimen is used to position specimen during testing (Scale marker is 1 mm per division.)

A 1-in. OD tube was infiltrated with nickel nitrate and fired under a similar heating schedule as described above, but in a 25% H₂ atmosphere to test the effect of atmosphere on consolidation. Metallography indicated that this tube was fully consolidated and that 25% H₂ is apparently an acceptable heat treating atmosphere.

A piece of tube was corrosion tested in a zinc and CaCl₂-KCl environment for 120 h at 800°C. This tube showed no apparent metallographic attack and a negligible weight gain, a SEM examination of a polished cross section (Fig. 7.8) showed no identifiable surface attack and no intergranular penetration, and no corrodent species could be found in the tungsten by x-ray analysis.

One of the crucibles was also corrosion tested as a container for an agitated mixture of molten zinc and fused CaCl₂-KCl at 800°C for 225 h. After cleaning in water and HCl to remove the salt and zinc from the crucible, no evidence of attack other than some minor surface staining was observed. Weight loss of the crucible was equivalent to 3.7 mils/year. These results appear most promising and indicate that plasma spraying can be used to fabricate both protective coatings and monolithic components such as crucibles and tubing for use in PDPM environments.

Tungsten CVD coatings. Segments of molybdenum spin-formed crucibles were sent to an outside vendor for deposition of a tungsten liner by chemical vapor deposition (CVD) methods. A set of six specimens with various thermomechanical histories was then analyzed metallographically to arrive at an optimum fabrication schedule. Parameters of interest were surface finish prior to tungsten deposition and heat-treatment temperatures after deposition. Heat treatments used included annealing in vacuum for 16 to 20 h at a temperature of 1000°C or at 1200°C. The tungsten layer was invariant to prior surface finish or heat treatment and consisted of large grains of high grain aspect ratio parallel to the deposition direction. In some cases, these grains may extend through the entire coating thickness.

Fig. 7.8. Scanning electron micrograph of a polished cross section of plasma-sprayed and nickel-treated tungsten after exposure to zinc and $\text{CaCl}_2\text{-KCl}$ for 120 h at 800°C . (Magnification, $1200\times$.)

The effect of prior surface finish was not metallographically observable except that one specimen of high interfacial roughness displayed some minor interfacial porosity. High-surface roughness may promote tungsten adhesion, but this hypothesis was not tested.

Heat treatment had a profound effect on the molybdenum substrate. The specimens receiving no treatment showed an as-drawn grain structure of moderately sized grains, slightly elongated in the circumferential direction, with fine highly disturbed grains at the interface where the molybdenum had been machined prior to tungsten deposition. The specimens treated at 1000°C showed somewhat coarser equiaxed grains with complete relief of the disturbed machined surface. The 1200°C specimens showed gross grain growth, which indicated a condition of excessive heat treatment.

It is suggested that the intermediate anneal (1000°C for 16–20 h) is optimal. The somewhat fine grain size should provide a strengthening effect, and the lesser extent of grain growth will possibly enhance intergranular strength. The untreated condition is probably unfavorable since the high apparent strains at the interface may promote delamination of the coating.

Tungsten metallization. Two tungsten-metallized alumina-yttria crucibles were fabricated for corrosion testing in Zn and $\text{CaCl}_2\text{-KCl}$ at a temperature of 800°C . One crucible was sectioned, and a coupon was tested in the zinc and salt environment for 120 h. The observed weight change after testing and cleaning in water and dilute HCl was negligible; no degradation was observed. Figure 7.9 shows a cross section of the exposed surface of this coupon after testing. No attack of the tungsten layer is observed, and no permeation of the zinc or salt into the coating has taken place. Post-test integrity of the coating and the coating-substrate interface is excellent.

A second crucible was tested in its original configuration as a container for an agitated zinc and salt mixture at 800°C for 250 h. The crucible was cooked, rinsed in water to

Fig. 7.9. Cross section of tungsten metallized layer (center) on alumina-yttria substrate (left) after exposure to zinc and $\text{CaCl}_2\text{-KCl}$ for 120 h at 800°C . (Area on the right is mounting material, Magnification, $600\times$.)

remove the salt layer, and sectioned without zinc removal. Macroscopic examination showed the crucible to be in excellent condition, and no degradation in the form of cracking or spallation of the coating was observed. A SEM examination (Fig. 7.10) showed no apparent surface degradation and no permeation of corrodents into the coating. A zinc x-ray map of the same area shows all zinc to be limited to the outer surface and the tungsten coating.

Fig. 7.10. An examination of tungsten crucibles by scanning electron microscope. (a) Tungsten metallized layer (middle) on alumina-yttria substrate (far left) after exposure to zinc and $\text{CaCl}_2\text{-KCl}$ for 120 h at 800°C , solidified zinc (right) is still in contact with tungsten; (b) zinc x-ray map illustrating lack of zinc permeation into tungsten layer. (Magnification, $1500\times$.)

Service life testing of crucibles with zinc. Three crucibles, a drawn and spun molybdenum crucible, a plasma-sprayed tungsten crucible (impregnated with nickel and sintered at 1300°C in hydrogen), and a molybdenum crucible (chemical vapor deposited with tungsten) are being tested in molten zinc at a temperature of 820°C. After 24 h, the molybdenum crucible showed no sign of corrosion.

Molybdenum crucibles, CVD coated with tungsten, appear to be very promising. One crucible has been thermal cycled at 100°C per h heatup and cooldown with no visual sign of coating separation. Sections of crucibles have been given thermal cycles of 16 h at 1000°C and 1200°C in a vacuum furnace to initiate a metallurgical bond between the tungsten coating and the molybdenum. The microstructure of these samples has been analyzed, and it is concluded that 16 h at 1000°C is a desirable thermal treatment. Although this treatment relieves the signs of stress in the surface grains of the molybdenum, it does not cause grain growth. There was no evidence that the thermal treatments created a metallurgical bond. The CVD tungsten coating appears to be mechanically bonded to the molybdenum, therefore, a rough surface appears to be advantageous for increasing bond strength during coating.

The plasma-sprayed tungsten crucible to be service life tested was impregnated with nickel nitrate and sintered at 1300°C in a 100% hydrogen atmosphere. There is some question regarding the availability of a 100% hydrogen atmosphere furnace large enough to sinter the full size crucible, therefore, samples were sintered in 25% hydrogen–75% nitrogen. Examination of samples sintered in the different hydrogen concentrations indicated that no difference in consolidation or porosity was seen; both appeared to be fully dense.

The plasma-sprayed tungsten crucible test ended in failure. Examination indicated that the cracks in the crucible were present while the zinc was in the molten state. To help prevent cracking in future plasma-sprayed tungsten crucibles, it is recommended to (1) incorporate curvature on the bottom, (2) increase the bottom thickness, and (3) control the heatup and cooldown rate at no greater than 100°C per hour.

There was no sign of corrosion on the plasma-sprayed tungsten crucible impregnated with nickel from the 4-d exposure to zinc. Therefore, this fabrication process still looks attractive for fabricating the full-size tungsten vessel.

References

1. R. H. Moore, U.S. Patent 2 948 486 (August 1960).
2. R. Eck, "Corrosion of Powder Metallurgy Molybdenum-Tungsten Alloys in Liquid Zinc," *European Symposium on Powder Metallurgy*, Stockholm, Sweden, June 4–8, 1978 (in German).
3. T. S. Toth and N. A. Lockington, *J. Less-Common Met.* 12, 353–65 (1967).
4. J. H. Brophy, L. A. Shepard, and J. Wulff, p. 113 in *Powder Metallurgy*, ed. by W. Leszynski, Interscience, New York (1961).
5. C. M. Edstrom, A. G. Phillips, L. D. Johnson, and R. R. Corle, *Literature on Fabrication of Tungsten for Application in Pyrochemical Processing of Spent Nuclear Fuels*, MTGM-78-51 (1979).
6. L. Brewer, *HP-67 Calculator Programs for Thermodynamic Data and Phase Diagram Calculations*, LBL-5485 (May 25, 1978).
7. L. Kaufman and H. Nesor, p. 179 in *Treatise on Solid State Chemistry*, Vol. 5, Plenum Press, New York (1975).

8. J. Belle and B. Lustman, *Properties of Uranium Dioxide*, WAPD-184 (1957).
9. C. A. Arenberg and P. Jahn, "Steam Sintering of Uranium Dioxide," *J. Am. Ceram. Soc.* **41** (5), 179 (1958).
10. R. J. Bard, J. P. Bertino, and D. L. Bunker, "Activating Uranium Dioxide," *Ind. and Eng. Chem.* **53** (12), 1003 (1961).
11. J. D. Christian, "Process Behavior and Control of Ruthenium and Cerium in Controlling Airborne Effluents from a Fuel Cycle Plant," Proceedings of the ANS-AIChE meeting, August 5-6 (1976).
12. B. J. Newby and D. W. Rhodes, *Ruthenium Behavior During Calcination*, ICP-1164 (1978).
13. J. H. Goode, *Voloxidation - Removal of Volatile Fission Products from Spent LMFBF Fuels*, ORNL/TM-3723 (1973).
14. T. R. Johnson, R. D. Pierce, L. Burris, Jr., and R. K. Steunenberg, *Skull Reclamation Process Part 2, Oxidation of Melt Refining Skulls*, ANL-6874 (1964).
15. P. Drossbach, p. 63 in *Elektrochemie Geschmolzener Salze*, Julius, Springer, Berlin (1933).
16. E. D. Eastman, D. D. Cubicciotti, and C. D. Thurmond, *The Chemistry and Metallurgy of Miscellaneous Materials*, ed. by L. L. Quill, McGraw-Hill, New York, 1950, pp. 6-12.
17. W. Eitel and B. Lange, *Z. Anorg. Allg. Chemie.* **171**, 168-810 (1928).
18. E. Heymann and E. Friedlander, *Z. Physik Chemie.* **A148**, 177-94 (1930).
19. R. Lorenz and D. Eitel, *Z. Anorg. Chemie.* **91**, 46-65 (1915).
20. C. R. Becker and T. S. Soine, *Screening Test for Proposed Molten Salt Electrolytes*, HW-77591, Hanford Atomic Products Operation (May 10, 1963).
21. J. A. Porter and A. E. Symonds, Jr., *Electrowinning Plutonium Metal*, TID-4500, Savannah River Laboratory (February 1966).
22. R. G. Auge, Rockwell International, Rocky Flats Plant, Golden, Colorado, private communication with T. D. Santa Cruz (May 1979).
23. R. A. Bailey and G. J. Janz, "Experimental Techniques in the Study of Fused Salts," in *The Chemistry of Non-Aqueous Solvents*, Vol. I, ed. by J. J. Lagowski, Academic Press, New York (1966).
24. T. R. Johnson, F. G. Teats, and R. D. Pierce, *A Method for the Purification of Molten Chloride Salts*, ANL-7603 (August 1969).
25. L. J. Mullins, Los Alamos Scientific Laboratories, personal communication with T. D. Santa Cruz (May 1979).
26. W. D. Burch et al., *Consolidated Fuel Reprocessing Program Progress Report for Period April 1 to June 30, 1979*, ORNL/TM-6994 (September 1979).
27. M. J. Steindler et al., *Fuel Cycle Program, Quarterly Progress Report January-March 1979*, ANL 79-45.
28. A. S. Yamamoto and W. Rostoker, *Trans. ASM* **50**, 1090 (1958).
29. Argonne National Laboratory, *Chemical Engineering Division, Fuel Cycle Program, Quarterly Progress Report, October-December 1978*, ANL 79-29.
30. B. Amecke, *Contributions to the Reprocessing of Thorium-Uranium Nuclear Fuels with the Salt Transport Method*, ANL-TRANS-1141 (1975).
31. M. D. Thompson and A. L. Kaye, "The Decomposition Potentials and Conductivities of Magnesium Oxide and of Alkaline Earths in Fused Fluorides," *Trans. Electrochem. Soc.* **67**, 169 (1935).
32. A. R. Gibson and J. H. Buddery in *Extraction and Refining of the Rarer Metals*, The Institution of Mining and Metallurgy, London (1957).

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